

## METHOD 8261

### VOLATILE ORGANIC COMPOUNDS BY VACUUM DISTILLATION IN COMBINATION WITH GAS CHROMATOGRAPHY/MASS SPECTROMETRY (VD/GC/MS)

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8261 is used to determine the concentrations of volatile organic compounds, and some low-boiling semivolatile organic compounds, in a variety of liquid, solid, and oily waste matrices, as well as animal tissues. This method is applicable to nearly all types of matrices regardless of water, soil, sediment, sludge, oil, and biota content. Method 8261 is useful in the determination of the following compounds:

| Compound                    | CAS Registry No. |
|-----------------------------|------------------|
| Acetone                     | 67-64-1          |
| Acetonitrile                | 75-05-8          |
| Acetophenone                | 98-86-2          |
| Acrolein                    | 107-02-8         |
| Acrylonitrile               | 107-13-1         |
| Allyl Chloride              | 107-05-1         |
| Aniline                     | 62-53-3          |
| Benzene                     | 71-43-2          |
| Bromochloromethane          | 75-97-5          |
| Bromodichloromethane        | 75-27-4          |
| Bromoform                   | 75-25-2          |
| Bromomethane                | 74-83-9          |
| 2-Butanone                  | 78-93-3          |
| <i>n</i> -Butylbenzene      | 104-51-8         |
| <i>sec</i> -Butylbenzene    | 135-98-8         |
| <i>tert</i> -Butylbenzene   | 98-06-6          |
| Carbon disulfide            | 75-15-0          |
| Carbon tetrachloride        | 56-23-5          |
| Chlorobenzene               | 108-90-7         |
| Chlorodibromomethane        | 124-48-1         |
| Chloroethane                | 75-00-3          |
| Chloroform                  | 67-66-3          |
| Chloromethane               | 74-87-3          |
| 2-Chlorotoluene             | 95-49-8          |
| 4-Chlorotoluene             | 106-43-4         |
| 1,2-Dibromo-3-chloropropane | 96-12-8          |

| Compound                            | CAS Registry No. |
|-------------------------------------|------------------|
| Dibromomethane                      | 74-95-3          |
| 1,2-Dichlorobenzene                 | 95-50-1          |
| 1,3-Dichlorobenzene                 | 541-73-1         |
| 1,4-Dichlorobenzene                 | 106-46-7         |
| <i>cis</i> -1,4-Dichloro-2-butene   | 764-41-0         |
| <i>trans</i> -1,4-Dichloro-2-butene | 110-57-6         |
| Dichlorodifluoromethane             | 75-71-8          |
| 1,1-Dichloroethane                  | 75-35-4          |
| 1,2-Dichloroethane                  | 107-06-2         |
| 1,1-Dichloroethene                  | 75-35-3          |
| <i>trans</i> -1,2-Dichloroethene    | 156-60-5         |
| <i>cis</i> -1,2-Dichloroethene      | 156-59-2         |
| 1,2-Dichloropropane                 | 78-87-5          |
| 1,3-Dichloropropane                 | 142-28-9         |
| 2,2-Dichloropropane                 | 594-20-7         |
| 1,1-Dichloropropene                 | 563-58-6         |
| <i>cis</i> -1,3-Dichloropropene     | 10061-01-5       |
| <i>trans</i> -1,3-Dichloropropene   | 10061-02-6       |
| Diethyl ether                       | 60-29-7          |
| 1,4-Dioxane                         | 128-91-1         |
| Ethyl acetate                       | 141-78-6         |
| Ethylbenzene                        | 100-41-4         |
| Ethyl methacrylate                  | 97-63-2          |
| Hexachlorobutadiene                 | 87-68-3          |
| 2-Hexanone                          | 591-78-6         |
| Iodomethane                         | 74-88-4          |
| Isobutyl alcohol                    | 78-83-1          |
| Isopropylbenzene                    | 98-82-8          |
| <i>p</i> -Isopropyltoluene          | 99-87-6          |
| Methacrylonitrile                   | 126-98-7         |
| Methylene chloride                  | 75-09-2          |
| Methyl methacrylate                 | 80-62-6          |
| 1-Methylnaphthalene                 | 90-12-0          |
| 2-Methylnaphthalene                 | 91-57-6          |
| 4-Methyl-2-pentanone                | 108-10-1         |
| Naphthalene                         | 91-20-3          |

| Compound                                   | CAS Registry No. |
|--|------------------|
| <i>N</i> -Nitrosodibutylamine              | 924-16-3         |
| <i>N</i> -Nitrosodiethylamine              | 55-18-5          |
| <i>N</i> -Nitrosodimethylamine             | 62-75-9          |
| <i>N</i> -Nitrosodi- <i>n</i> -propylamine | 621-64-7         |
| <i>N</i> -Nitrosomethylethylamine          | 10595-95-6       |
| Pentachloroethane                          | 76-01-7          |
| 2-Picoline                                 | 109-06-8         |
| Propionitrile                              | 107-12-0         |
| <i>n</i> -Propylbenzene                    | 103-65-1         |
| Pyridine                                   | 110-86-1         |
| Styrene                                    | 100-42-5         |
| 1,1,2,2-Tetrachloroethane                  | 79-34-5          |
| Tetrachloroethene                          | 127-18-4         |
| Tetrahydrofuran                            | 109-99-9         |
| Toluene                                    | 108-88-3         |
| <i>o</i> -Toluidine                        | 95-53-4          |
| 1,2,3-Trichlorobenzene                     | 87-61-6          |
| 1,2,4-Trichlorobenzene                     | 120-82-1         |
| 1,1,1-Trichloroethane                      | 71-55-6          |
| 1,1,2-Trichloroethane                      | 79-00-5          |
| Trichloroethene                            | 79-01-6          |
| Trichlorofluoromethane                     | 75-69-4          |
| 1,2,3-Trichloropropane                     | 96-18-4          |
| 1,2,4-Trimethylbenzene                     | 95-63-6          |
| 1,3,5-Trimethylbenzene                     | 108-67-8         |
| Vinyl chloride                             | 75-00-3          |
| <i>o</i> -Xylene                           | 95-47-6          |
| <i>m</i> -Xylene                           | 108-38-3         |
| <i>p</i> -Xylene                           | 106-42-3         |

1.2 This method can be used to quantitate most volatile organic compounds that have a boiling point below 245°C and a partition coefficient below 15,000, which includes compounds that are miscible with water. Note that this range includes compounds not normally considered to be volatile analytes (e.g., nitrosamines, aniline, and pyridine).

1.3 Method detection limits (MDLs) are provided in Table 8. These values are provided for guidance in developing appropriate quantitation limits. Each laboratory should develop its own matrix-specific quantitation limits using the guidance found in Chapter One. Samples that require dilution will have proportionately higher detection limits.

1.4 Method 8261 is based on a vacuum distillation and cryogenic trapping procedure (Method 5032) followed by gas chromatography/mass spectrometry (GC/MS). The method incorporates surrogate-based matrix correction, where the analysis of multiple samples is used to predict matrix effects by employing specific surrogates. As a result, the calculations involved are specific to Method 8261, and may not be used with data generated by another method. This method includes all of the necessary steps from sample preparation through instrumental analysis.

1.5 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two, Sec. 2.1, for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.6 This method is restricted to use by, or under the supervision of, experienced personnel who are familiar with the techniques of vacuum distillation and experienced in the use of gas chromatography and mass spectrometry. Each analyst must demonstrate the ability to generate acceptable results with this method.

## 2.0 SUMMARY OF METHOD

2.1 An aliquot of a liquid, solid, or tissue sample is transferred to a sample flask, which is then attached to the vacuum distillation apparatus (see Figure 1). Nominal sample sizes are 5 mL for water, 5 g for soil, 5 g for tissue, and 0.2 to 1 g for oil. The sample sizes may be varied, depending on analytical requirements, while using the same calibration curve. The surrogate corrections will compensate for variations in sample size. A total of 5 mL of reagent water is added to the aliquot of soil, tissue, or oil.

2.2 The sample chamber pressure is reduced using a vacuum pump and remains at approximately 10 torr (the vapor pressure of water) as water is removed from the sample. The vapor is passed over a condenser coil chilled to 5°C, which results in the condensation of water vapor. The uncondensed distillate is cryogenically trapped in a section of stainless steel tubing chilled to the temperature of liquid nitrogen (-196°C).

2.3 After an appropriate distillation period, which may vary due to matrix or analyte group, the condensate contained in the cryotrap is thermally desorbed and transferred to the gas chromatograph using helium as a carrier gas.

2.4 Analytes eluted from the gas chromatographic column are introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source).

2.5 Quantitation is accomplished in three specific steps.

2.5.1 The first step is the determination of the response of each analyte at the mass spectrometer using external standard means. The amount (mass) of analyte introduced into the mass spectrometer is determined by comparing the response (area) of the quantitation ion for the analyte from a sample analyses to the quantitation ion response generated during the initial calibration.

2.5.2 The second step is the determination of surrogate recovery. The recommended surrogates are listed in Table 3. The recovery of each analyte can be predicted using the recovery-properties relationship solutions (see Sec. 12.8).

2.5.3 Finally, using the predicted recovery, sample size, and quantity of analyte detected at the mass spectrometer, the concentration of analyte is calculated.

2.6 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

2.7 It must be emphasized that the vacuum distillation conditions are optimized to remove analyte from the sample matrix and to isolate water from the distillate. The conditions may be varied to optimize the method for a given analyte or group of analytes. The length of time required for distillation may vary due to matrix effects or the analyte group of interest. Operating parameters may be varied to achieve optimum analyte recovery.

### 3.0 DEFINITIONS

Many of the terms used in this method are defined in Chapter One. Other terms specific to this procedure are listed in the glossary at the end of the method.

### 4.0 INTERFERENCES

4.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baseline in the chromatograms.

4.1.1 Interferences distilled from the sample will vary from source to source, depending on the particular sample or matrix. The analytical system should be checked to insure freedom from interferences by analyzing method blanks utilizing the identical analytical conditions used for samples.

4.1.2 The apparatus can be decontaminated with a ten-minute evacuation of the distillation apparatus while the condenser coils are heated to 45°C or higher.

4.2 The laboratory where the analysis is to be performed should be completely free of solvents. Many common solvents, most notably acetone and methylene chloride, are frequently found in laboratory air at low levels. The sample receiving chamber should be loaded in a clean environment to eliminate the potential for contamination from ambient sources.

4.3 Samples may be contaminated during shipment. Field and trip blanks should be analyzed to insure integrity of the transported sample. It is recommended that wherever possible, sample aliquots and surrogates are transferred directly to sample flasks in the field, weighed and sealed using Viton® (or equivalent) O-ring connections.

4.4 Impurities in purge gas and from organic compounds out-gassing from plumbing account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by including laboratory reagent blanks. All gas lines should be equipped with traps to remove hydrocarbons and oxygen.

## 5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 The following analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, trichloroethene, vinyl chloride, 1,1,2-trichloroethane, *N*-Nitrosodibutylamine, *N*-Nitrosodiethylamine, *N*-Nitrosodimethylamine, *N*-Nitrosodi-*n*-propylamine, and *N*-Nitrosomethylethylamine. Pure standard materials and stock standard solutions containing these compounds should be handled in a hood and a NIOSH/MESA-approved toxic gas respirator should be worn when the analyst handles high concentration solutions of these compounds.

5.3 This method employs liquid nitrogen as a cryogenic coolant. Liquid nitrogen can cause burns to exposed skin, and should be handled with care. Employ insulated gloves or tongs when using this material.

## 6.0 EQUIPMENT AND SUPPLIES

6.1 Microsyringes - 10-μL, 25-μL, 100-μL, 250-μL, 500-μL, and 1000-μL. Each of these syringes should be equipped with a 20-gauge (0.006 in ID) needle.

6.2 Syringe - 5-mL and 10-mL gas-tight, with Luer Lock tip and needles.

### 6.3 Balances

6.3.1 Analytical balance capable of accurately weighing 0.0001 g.

6.3.2 Top-loading balance capable of weighing 0.1 g.

6.4 Balance weights - Stainless steel S-class weights ranging from 5 mg to 100 g.

6.5 Sample flask - 100-mL borosilicate bulb joined to a 15-mm ID borosilicate O-ring connector, or equivalent. The flask must be capable of being evacuated to a pressure of 10 millitorr without implosion. The flask is sealed for sample storage with an O-ring capable of maintaining the vacuum in the chamber, a 15-mm ID O-ring connector cap, and a pinch clamp.

6.6 Vacuum distillation apparatus (See Figure 1) - The basic apparatus consists of a sample chamber connected to a condenser which is attached to a heated six-port valve (V4) and is available from Cincinnati Analytical Instruments, Cincinnati, OH. The sampling valve is connected to the following;

- 1) condenser (by way of vacuum pump valve - V3)
- 2) vacuum pump
- 3) cryotrap
- 4) gas chromatograph/mass spectrometer

The six-port sampling valve (V4) should be heated to at least 120°C to prevent condensation and potential carryover.

6.6.1 The condenser is operated at two different temperatures. The lower temperature is between -5 and 10°C, and the upper temperature is greater than 45°C. The lower temperature is used to condense water and should be a consistent temperature throughout the interior surface. The condenser is heated to the upper temperature to remove water and potential contaminants. The initial apparatus described in Reference 9 used circulating fluids (see Fig 1) but other means of controlling temperatures may be used.

6.6.2 The apparatus is heated to a temperature sufficient to prevent condensation of analytes onto condenser walls, valves, and connections. The transfer line from the sampling valve to the gas chromatograph should be heated to a temperature between 150°C and the upper temperature utilized by the GC program.

6.6.3 Pirani gauges are recommended at the vacuum pump for monitoring the distillation (Edwards Pirani gauge model 1001 with Pirani gauge head model PRH10K, or equivalent).

6.6.4 The original apparatus used a cryoloop consisting of an 8-in length of 1/8-in OD stainless steel tubing without any packing. These dimensions are not critical, but the loop must be of dimensions sufficient to trap the analytes of concern. Shorter loops will trap the most volatile analytes less effectively. Revised performance criteria should be determined whenever the dimensions of the cryoloop are changed significantly.

6.6.5 The dimensions of the initial apparatus have been published in Reference 5. These dimensions are not critical and can be varied without altering the results (i.e., 6-

port valves versus combinations of other valves, different condenser sizes, vacuum pump capacity). Any apparatus used must demonstrate appropriate performance for the intended application (see Tables 6-9).

## 6.7 Gas chromatograph/mass spectrometer system

6.7.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

6.7.2 Column - 60 m x 0.53-mm ID, 3.0- $\mu$ m film thickness VOCOL fused-silica capillary column (Supelco, Bellefonte, PA), or equivalent. Laboratories may use other columns provided that they document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

6.7.3 Mass spectrometer - Capable of scanning from 35-350 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets the criteria listed in Table 1 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the gas chromatograph inlet.

6.7.4 Gas chromatograph/mass spectrometer heated jet separator interface - A heated glass jet separator interface capable of removing from 10 to 40 mL/min of helium from the exit end of the wide-bore capillary column. The interface should have the ability to be heated through a range of 100 to 220°C.

6.8 Containers for liquid nitrogen - Dewars or other containers suitable for holding the liquid nitrogen used to cool the cryogenic trap and sample loop.

## 7.0 REAGENTS AND SUPPLIES

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

7.3 Methanol -  $\text{CH}_3\text{OH}$ , purge-and-trap grade, or equivalent. Store away from other solvents.

7.4 Standard solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

7.4.1 Place about 9.8 mL of methanol in a 10-mL tared, ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.



7.4.2 Add the assayed reference material, as described below.

7.4.2.1 Liquids - Using a 100- $\mu$ L syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

7.4.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side-arm relief valve and direct a gentle stream of gas onto the methanol meniscus.

7.4.3 Reweigh, dilute to volume, stopper, and mix by inverting the flask several times. Calculate the concentration in micrograms per microliter ( $\mu\text{g}/\mu\text{L}$ ) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.4.4 Transfer the stock standard solution into a PTFE-sealed screw cap bottle. Store, with minimal headspace, at -10 to -20°C and protect from light.

7.4.5 Prepare fresh gas standards every two months. Reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently. All other standards should be replaced after six months, or sooner if comparison with check standards indicates a problem.

7.5 Secondary dilution standards - Using stock standard solutions, prepare in methanol secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

## 7.6 Surrogate standards

This method incorporates surrogates that are added to each sample prior to analysis and are used to monitor and correct for matrix effects such as gas-liquid partitioning and condensation. Additional surrogates are used to monitor the effectiveness of the surrogate corrections. The specific surrogates used are described in the following sections. Additional information is provided in the glossary. A stock solution containing all of the surrogates should be prepared in methanol at the concentrations listed in Table 3 (15-150 ng/mL). Each sample should be spiked with 5  $\mu\text{L}$  of the surrogate spiking solution prior to analysis.

7.6.1 Gas-liquid partitioning surrogates ( $\alpha$ -surrogates) - The following compounds are recommended for use as  $\alpha$ -surrogates:

|   |                                  |
|---|----------------------------------|
| Hexafluorobenzene   | 1,2-Dichloroethane- $d_4$        |
| Pentafluorobenzene  | 1,2-Dibromoethane- $d_4$         |
| Fluorobenzene   | Ethyl acetate- $^{13}\text{C}_2$ |
| 1,4-Difluorobenzene   | Acetone- $d_6$                   |
| <i>o</i> -Xylene- $d_{10}$                                      | 1,4-Dioxane- $d_8$               |
| Chlorobenzene- $d_5$ (may also be used as a $\beta$ -surrogate) | Pyridine- $d_5$                  |

7.6.2 Condensation surrogates (boiling point or  $\beta$ -surrogates) - The following compounds are recommended for use as  $\beta$ -surrogates:

|   |                               |
|---|-------------------------------|
| Toluene- $d_8$  | 1,2,4-Trichlorobenzene- $d_3$ |
| Chlorobenzene- $d_5$ (may also be used as an $\alpha$ -surrogate) | 1,2-Dichlorobenzene- $d_4$    |
| Bromobenzene- $d_5$   | 1-Methylnaphthalene- $d_{10}$ |
| Decafluorobiphenyl  |                               |

### 7.6.3 Additional surrogates

Additional surrogates (check surrogates) should be analyzed to monitor the effectiveness of the matrix corrections. The recommended check surrogates are listed below, along with the aspects of the vacuum distillation process that they may be used to evaluate.

7.6.3.1 Benzene- $d_6$ , 1,1,2-trichloroethane- $d_3$ , and 1,2-dichloropropane- $d_6$  are low-boiling, volatile analytes. Their recoveries represent the adequacy of the relative volatility-recovery relationship for most analytes.

7.6.3.2 Methylene chloride- $d_2$  is similar to benzene- $d_6$  and 1,2-dichloropropane- $d_6$  (see Sec. 7.6.3.1), but is more sensitive to the presence of excessive methanol. Low recovery of this analyte may indicate a large amount of polar solvents in a sample.

7.6.3.3 Diethyl ether- $d_{10}$  is a volatile low-boiling surrogate that coelutes with methanol. This compound is used to identify when the concentration of methanol begins to affect the GC/MS determination step.

7.6.3.4 4-Bromo-1-fluorobenzene and naphthalene- $d_8$  are higher-boiling analytes and their recoveries are an indication of the adequacy of corrections for their boiling-point range.

7.6.3.5 Acetophenone- $d_5$  and nitrobenzene- $d_5$  are higher-boiling and less volatile analytes and their recoveries are an indication of the adequacy of matrix corrections for the less volatile analytes.

7.6.3.6 Acetone- $d_6$  is used to check the adequacy of the surrogate corrections for the less volatile analytes.

7.6.3.7 Ethyl acetate- $^{13}\text{C}_2$  is a less volatile analyte that has been observed to degrade in some media and is also affected by the presence of methanol. Its recovery should be considered with the recovery of other surrogates.

7.6.3.8 Pyridine- $d_5$  is the least volatile of the surrogates and its recovery is an excellent indication of the limits of the method. It is very sensitive to matrix variations and can be poorly (or excessively) recovered when all other surrogates (and analytes) are recovered adequately.

7.7 4-Bromofluorobenzene (BFB) standard - A solution containing 25 ng/ $\mu\text{L}$  of BFB in methanol should be prepared. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then a more dilute BFB standard solution may be required.

## 7.8 Calibration standards

Calibration standards at a minimum of five concentrations should be prepared from the secondary dilution of stock standards (see Sections 7.1 and 7.2). Prepare these solutions in reagent water or purge-and-trap grade methanol. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Store for one week or less at  $-10$  to  $-20^\circ\text{C}$  in a vial with minimal headspace.

7.8.1 It is the intent of EPA that all target analytes for a particular analysis be included in the calibration standard(s). These target analytes may not include the entire list of analytes (see Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

7.8.2 The calibration standards must also contain the surrogates chosen for the analysis.

7.9 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards be stored at  $-10$  to  $-20^\circ\text{C}$  in screw-cap or crimp-top amber bottles with PTFE liners.

7.10 Liquid nitrogen - For use in cooling the cryogenic trap (see Figure 1) and the condenser described in Reference 9, if employed.

## 8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

8.2 Aqueous samples should be stored with minimal or no headspace to minimize the loss of highly volatile analytes.

8.3 Samples to be analyzed for volatile compounds should be stored separately from standards and other samples.

## 9.0 QUALITY CONTROL

9.1 Refer to Chapter One and Method 8000 for specific quality control procedures. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

9.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows and calibration verification. In addition, the initial calibration and calibration verification data must be evaluated as described below.

9.2.1 The GC/MS must be tuned to meet the BFB criteria in Table 1, each 12-hour period during which analyses are performed.

9.2.2 The GC/MS must undergo an initial calibration, as described in Sec. 10.3.

9.2.3 A system performance check should be made before the initial calibration data are used. The surrogates chlorobenzene- $d_5$ , 1,2-dichlorobenzene- $d_4$ , and tetrahydrofuran- $d_8$  are used as reference compounds against which other analytes are evaluated as relative responses. This provides assurance that the system is sufficiently sensitive to determine the analytes presented in Table 2. There are four classes of compounds that are determined using this method. Class I compounds include those compounds with boiling points generally below 160 °C and  $\alpha$ -values (or K-values) below 50 (i.e., the permanent gases and volatiles). Class II compounds are those with boiling points greater than 160 °C (i.e., the neutral semivolatiles). Class III compounds are those with  $\alpha$ -values greater than 50 (i.e., the water soluble volatiles). Class IV compounds are the basic compounds that are susceptible to degradation and have a low detector response (i.e., the basic semivolatiles).

9.2.3.1 Class I compounds are monitored using four compounds (the System Performance Check Compounds, or SPCCs for Class I) that are checked for a minimum average response relative to chlorobenzene- $d_5$ . These compounds are chloromethane, 1,1-dichloroethane, bromoform, and 1,1,2,2-tetrachloroethane. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Example problems include:

9.2.3.1.1 Chloromethane is an analyte likely to be lost if the cryotrap is not properly cooled or if there is a significant air leak in the system.

9.2.3.1.2 Bromoform is a compound that can be poorly recovered if the system is under a required vacuum or there are significant cold spots.

9.2.3.1.3 1,1,2,2-Tetrachloroethane and 1,1-dichloroethane may be degraded in the apparatus or by system contamination.

9.2.3.1.4 The minimum mean relative responses for the various Class I SPCCs are as follows:

|                           |      |
|---------------------------|------|
| Chloromethane             | 0.05 |
| 1,1-Dichloroethane        | 0.10 |
| Bromoform                 | 0.10 |
| 1,1,2,2-Tetrachloroethane | 0.30 |

9.2.3.2 Class II compounds are monitored using two compounds (SPCCs for Class II) that are checked for a minimum average response relative to 1,2-dichlorobenzene- $d_4$ . These compounds are hexachlorobutadiene, and 2-methyl-naphthalene.

9.2.3.2.1 Hexachlorobutadiene is likely to be lost if there is a cold spot or degradation due to system contamination.

9.2.3.2.2 2-Methyl naphthalene is very sensitive to cold spots and contamination.

9.2.3.2.3 The minimum mean relative responses for the Class II SPCCs are as follows:

|                     |      |
|---------------------|------|
| Hexachlorobutadiene | 0.30 |
| 2-Methylnaphthalene | 0.30 |

9.2.3.3 Class III compounds are monitored using two compounds (SPCCs for Class III) that are checked for a minimum average response to tetrahydrofuran- $d_8$ . These compounds are 1,4-dioxane and pyridine.

9.2.3.3.1 1,4-Dioxane can be lost due to a poor system vacuum. The compound may also have a low response due to poor chromatography.

9.2.3.3.2 Pyridine can be lost due to poor system vacuum and system contamination. Too much water in the cryoloop will also depress the relative response.

9.2.3.3.3 The minimum mean relative responses for the Class III SPCCs are as follows:

|             |      |
|-------------|------|
| 1,4-Dioxane | 0.10 |
| Pyridine    | 0.10 |

9.2.3.4 Class IV compounds are monitored using two compounds (SPCCs for Class IV) and are checked for a minimum average response relative to tetrahydrofuran- $d_8$ . These compounds are aniline, *N*-nitrosodimethylamine and *N*-nitrosodiethylamine.

9.2.3.4.1 Each of the SPCCs for Class IV is easily lost if there is a poor vacuum, system contamination, or active sites. The SPCC compounds may also have low responses due to poor chromatography.

9.2.3.4.2 The minimum mean relative responses for the Class III SPCCs are as follows:

|                                |       |
|--------------------------------|-------|
| Aniline                        | 0.010 |
| <i>N</i> -Nitrosodimethylamine | 0.005 |
| <i>N</i> -Nitrosodiethylamine  | 0.010 |

9.2.4 The Calibration Check Compound (CCC) data must be evaluated before the initial calibration data are employed. As with the SPCC criteria, the CCC criteria are based on four classes of compounds (I-IV). The CCCs are evaluated on the basis of the relative standard deviation (RSD) of the calibration factors of each compound determined by an external standard calibration procedure. Calculate the standard deviation and relative standard deviation (RSD) of the calibration factors for each compound in the initial calibration, as described in Sec. 12.4.

9.2.4.1 The CCCs for the Class I compounds are:

Vinyl chloride  
Chloroform  
Toluene  
Ethylbenzene  
1,2-Dichloroethane  
Bromobenzene

In practice, the calculated RSD for each Class I CCC should be  $\leq 20\%$ , and it must be  $\leq 35\%$ .

9.2.4.2 The CCCs for the Class II compounds are:

1,3-Dichlorobenzene  
1,2,3-Trichlorobenzene  
Naphthalene

In practice, the calculated RSD for each Class II CCC should be  $\leq 25\%$  and it must be  $\leq 35\%$ .

9.2.4.3 The CCCs for the Class III compounds are:

4-Methyl-2 pentanone  
Methacrylonitrile  
1,4-Dioxane

In practice, the calculated RSD for each Class III CCC should be  $\leq 30\%$  and it must be  $\leq 40\%$ .

9.2.4.4 The CCCs for the Class IV compounds are:

*N*-Nitrosomethylethylamine

*N*-Nitrosodi-*n*-propylamine

In practice, the calculated RSD for each Class IV CCC should be  $\leq 35\%$  and it must be  $\leq 45\%$ .

9.2.4.5 If any CCC fails the criteria listed in Secs. 9.2.4.1 - 9.2.4.4, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

9.2.5 Initial calibration linearity

9.2.5.1 If the RSD of the calibration factors for any compound is 20% or less, then the instrument response is assumed to be constant over the calibration range, and the average calibration factor may be used for quantitation (Secs. 12.3 and 12.8.5).

9.2.5.2 If the RSD of the calibration factors for any compound is greater than 20%, see Sec. 7.0 in Method 8000 for options on dealing with non-linear calibrations. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

9.2.5.3 When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

NOTE: The RSD is used as a measure of linearity of each compound's response irrespective of the CCC criteria in Sec. 9.2.4. If the CCC criteria are met, then the results from the initial calibration may be used to calculate subsequent sample results. However, the calculations for each analyte must take into account the linearity of the calibration factors for that analyte in determining which of the calibration approaches described in Method 8000 are to be employed.

9.2.6 GC/MS calibration verification

A calibration verification must be performed for all samples analyzed after the 12-hour analytical shift during which the initial calibration was performed.

9.2.6.1 Prior to the analysis of samples, inject or introduce 5-50 ng of the 4-bromofluorobenzene standard into the GC/MS system using the same introduction method as is used for samples. The resultant mass spectra for the BFB must meet the criteria given in Table 1 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

9.2.6.2 The initial calibration curve (Sec. 9.2.2) for each compound of interest must be verified once every 12 hours during analysis, using the introduction technique used for samples. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS and by checking the SPCCs and CCCs, as described in Sec. 10.5.

NOTE: A method blank should be analyzed prior to the calibration standard to ensure that the total system (introduction device, transfer lines, and GC/MS system) is free of contaminants.

#### 9.2.6.3 System performance check compounds (SPCCs)

A system performance check must be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Secs. 9.2.3.1 - 9.2.3.4). This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

#### 9.2.6.4 Calibration check compounds (CCCs)

9.2.6.4.1 After the system performance check is met, the CCCs listed in Secs. 9.2.4.1 - 9.2.4.4 are used to check the validity of the initial calibration. Calculate the percent difference as described in Sec. 12.5.

9.2.6.4.2 If the percent difference for each CCC is  $\leq 35\%$  for the Class I and Class II CCCs,  $\leq 40\%$  for the Class III CCCs, and  $\leq 45\%$  for the Class IV CCCs, then the initial calibration is assumed to be valid, and analyses may continue. If the criteria are not met for any one CCC, then corrective action must be taken prior to the analysis of samples.

9.2.6.4.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new five-point initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

9.2.7 The responses of the surrogates and their retention times must be evaluated immediately after or during data acquisition. If the retention time for any surrogate changes by more than 30 seconds from the last calibration verification (12 hours), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the surrogates changes by a factor of two (-50% to +100%) from the previous calibration verification standard, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.



9.3 Initial demonstration of proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

9.4 Sample quality control for preparation and analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection/quantitation limit). At a minimum, this includes the analysis of QC samples including a method blank and a laboratory control sample (LCS) in each analytical batch, the addition of surrogates to each field sample and QC sample, and routine analyses of matrix spike and matrix spike duplicate aliquots.

9.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

9.4.2 The various surrogates added to the sample are used to document the effect of the sample matrix on the overall analysis. Therefore, the use of matrix spike/matrix spike duplicate samples is not necessary.

9.4.3 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. When the surrogate recoveries in a sample indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

#### 9.5 Surrogate recoveries

The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on developing and updating surrogate limits. Matrix effects and distillation performance may be monitored separately through the use of surrogates. The effectiveness of using the  $\alpha$ - and  $\beta$ -surrogates to correct matrix effects is monitored using the check surrogates identified in Sec. 7.6.3.

9.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

9.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the

needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Establish the GC/MS operating conditions, using the following information as guidance. Optimize the conditions for selectivity and sensitivity. Once established, the same operating conditions must be used for all analyses, including calibrations, blanks, and samples.

Recommended GC/MS operating conditions:

|                             |   |
|-----------------------------|---|
| Electron energy:            | 70 volts (nominal)                                |
| Mass range:                 | 38-270 amu  |
| Scan time:                  | To give 8 scans/peak but not to exceed 3 sec/scan |
| Jet separator temperature:  | 210°C   |
| Transfer line temperature:  | 280°C   |
| Injector inlet temperature: | 240°C   |
| Inlet pressure:             | 10 psi  |
| Initial column temperature: | 10°C  |
| Initial hold time:          | 3.0 min   |
| Temperature Program #1:     | 50°C/min to 40°C                                  |
| Temperature Program #2:     | 5°C/min to 120°C                                  |
| Temperature Program #3:     | 20°C/min to 220°C                                 |
| Final column temperature:   | 220°C   |
| Final hold time:            | 3.4 min   |

10.2 Prior to the initial calibration, the GC/MS system must be hardware-tuned to meet the criteria in Table 1 for a 5-50 ng injection of 4-bromofluorobenzene (2-μL injection of the BFB standard). Analyses must not begin until these criteria are met.

### 10.3 Initial calibration

As with techniques such as purge-and-trap GC/MS, the initial calibration involves carrying the calibration standards through the entire distillation and analysis procedure.

10.3.1 Cool the cryoloop to -150°C (or lower) while the sample loop valve is in the load position (Valve V4 in Figure 1).

10.3.2 Cool the condenser column to the recommended temperature for vacuum distillation operation (-5 to + 5°C).

10.3.3 Close the valve to the sample chamber (Valve V1 in Figure 1).

10.3.4 Add 5 mL of reagent water to the sample flask and spike the water with the appropriate standards and surrogates, and reconnect the flask to the apparatus.

10.3.5 Perform the vacuum distillation and introduce the distillate into the GC/MS, as described in Sec. 11.2.

10.3.6 Repeat the procedure for the remaining calibration standards.

#### 10.4 Calibration factors

Calculate a calibration factor (CF) for each target analyte and surrogate in each of the five initial calibration standards as described in Sec. 12.1, using external standard calibration techniques (see Method 8000). Calculate the relative response (RR) for each SPCC in the calibration standards, as described in Sec. 12.2.

#### 10.5 Calibration verification

The initial calibration must be verified at the beginning of each 12-hour analytical shift during which samples are to be analyzed. The verification involves the analysis of the mid-concentration standard from the initial calibration, using the procedures described in Secs. 10.3.1 to 10.3.5.

10.5.1 Prior to the analysis of standards, blanks, or samples, the GC/MS system must be hardware tuned to meet the criteria in Table 1 for BFB.

10.5.2 For each analyte in the calibration verification standard, calculate the calibration factor, as described in Sec. 12.1. Calculate the relative response for each SPCC in the calibration verification standard, as described in Sec. 12.2.

10.5.3 Evaluate the SPCCs and CCCs as described in Secs. 9.2.6.3 and 9.2.6.4. The analysis of samples should not proceed until the calibration has been verified.

### 11.0 PROCEDURE

#### 11.1 Sample preparation

Other sample volumes or weights may be employed, provided that the sensitivity of the method is adequate for project needs. Given the inherent recovery correction, changes in sample size do not necessitate recalibration of the instrument.

##### 11.1.1 Aqueous samples

Quickly transfer a 5-mL aliquot of the sample to the distillation flask, taking care not to introduce air bubbles or agitate the sample during the transfer. Add 10  $\mu$ L of the surrogate spiking solution to the sample in the flask, and attach the flask to the vacuum distillation apparatus.

##### 11.1.2 Solid and soil samples

Solid and soil samples should be rapidly withdrawn from their sample container and weighed while still cold. Weigh out a 5-g aliquot and then rapidly transfer it to the sample chamber. Add 10  $\mu$ L of the surrogate spiking solution to the sample in the flask, and attach the flask to the vacuum distillation apparatus.

11.1.2.1 Determination of percent dry weight - When sample results are to be calculated on a dry weight basis, a second portion of sample should be weighed at the same time as the portion used for analytical determination.

**WARNING:** The drying oven should be contained in a hood or be vented. Significant laboratory contamination may result from drying a heavily contaminated sample.

Immediately after weighing the sample for extraction, weigh 5 - 10 g of the sample into a tared crucible. Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as described in Sec. 12.6.

11.1.2.2 It is highly recommended that the sample aliquot for dry weight determination not be withdrawn from the sample container until it is certain that no analytical samples will be needed for high concentration analysis. This is to minimize loss of volatiles and to avoid sample contamination from the laboratory atmosphere.

#### 11.1.3 Tissue samples

Tissue samples which are fleshy may have to be minced into small pieces to get them through the neck of the sample chamber. This is best accomplished by freezing the sample in liquid nitrogen before any additional processing takes place. Biota containing leaves and other softer samples may be minced using clean scissors. Weigh out a 5-g aliquot and then rapidly transfer it to the sample chamber. Add 10 µL of the surrogate spiking solution to the sample in the flask, and attach the flask to the vacuum distillation apparatus.

#### 11.1.4 Oil samples

Weigh out 0.2 to 1.0 g of oil, and then rapidly transfer it to the sample chamber. Add 10 µL of the surrogate spiking solution to the sample in the flask, and attach the flask to the vacuum distillation apparatus.

### 11.2 Analysis

11.2.1 Turn the coolant/heat valve (V2 in Fig. 1) to circulate coolant through the condenser coils. Be sure all connections are complete and sealed properly. Open the sample chamber valve to begin the distillation. Continue distillation for 5-10 minutes.

**NOTE:** IF PIRANI GAUGES ARE USED, after five minutes of distillation, the Pirani gauge at the vacuum pump should indicate  $\leq 0.1$  torr. If this pressure is not attained, a leak may be present and the distillation may not be successful. Distillation performance surrogates should be evaluated for acceptability of distillation.

11.2.2 Setup the data system for acquisition of the data file. This may be done prior to 11.2.1. While distillation times may vary depending on sample matrix, the data system should be ready and the GC oven should be at equilibrium by the time the distillation is complete.

11.2.3 GC/MS analyses may be performed once the distillation is complete. Turn the sampling valve handle to the inject position while maintaining the cryoloop at -150°C or lower. Begin heating the cryoloop and desorb the sample in the loop. Commence GC/MS data acquisition.

11.2.4 Once acquisition has begun, the sample chamber valve may be closed and the sample flask removed.

11.2.5 The distillation apparatus can now be readied for the next analyses. This is accomplished by switching the vacuum pump valve (V3 in Fig. 1) to the vacuum pump position which disconnects the vacuum stream to the sampling valve (V4 in Fig. 1). The condenser is heated to the decontamination temperature recommended by the manufacturer. Evacuate the distillation apparatus for 10 minutes.

## 12.0 DATA ANALYSIS AND CALCULATIONS

The quantitation routine employed in Method 8261 differs significantly from that used in Method 8260 (using the Method 5032 sample preparation). Where Method 8260 uses one internal standard to correct injection/preparation variations for a given analyte, Method 8261 uses a series of surrogates to define the relationships of compound recoveries to their physical properties. Those relationships are used to extrapolate target analyte recoveries. Each target analyte and surrogate is calibrated using an external standard calibration procedure. The concentration of the analyte in the sample is determined using the predicted analyte recovery, sample size, and amount of analyte detected by the mass spectrometer. The relationships are solved using multiple surrogates and the errors associated with these relationships can be calculated and can be used as indicators of data accuracy for the analyses. The quantitation limits for those analytes that are not detected are also corrected to reflect matrix effects.

The quantitation algorithms and sequence presented here have been demonstrated to be acceptable and can be accomplished easily in a spreadsheet format (Reference 7). The quantitation routine presented is a stepwise procedure that initially estimates the  $\alpha$ -effects on the  $\beta$ -surrogates, calculates the boiling point effects, and then calculates the relative volatility effects. After the analyte recoveries are calculated, the amount of analyte detected by the mass spectrometer is corrected by the recovery and sample size to provide the analyte concentration. Table 3 lists the  $\alpha$ - and  $\beta$ -surrogates. Additional surrogates can be used to improve the solution of the matrix effects-recovery relationship.

Other surrogate correction approaches may be employed when they have been demonstrated to improve the assessment of matrix effects. Large samples of biota (10 g or more) may require that the analyst address the partitioning of analytes between air and the organic phase. Such an approach is described in References 8 and 9.

### 12.1 Calculation of calibration factors

The response of the mass spectrometer to a given concentration of a surrogate or target analyte is used to calculate a calibration factor (CF) in a fashion analogous to the external calibration procedures used in GC methods.

The following equation is used to calculate the calibration factor for each target analyte and surrogate.

$$\text{Calibration factor} = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Amount of the Compound Injected (in nanograms)}}$$

## 12.2 Calculation of relative response for SPCCs

The relative response (RR) is simply the ratio of the response of an SPCC to the response of the surrogate compound used as a reference (see Table 3), calculated as shown below:

$$\text{Relative response} = \frac{\text{CF of SPCC}}{\text{CF of the surrogate compound}}$$

12.3 Calculate the mean RR for each SPCC using the five RR values from the initial (5-point) calibration curve in Sec. 12.2, as follows:

$$\text{mean RR} = \frac{\sum_{i=1}^n \text{RR}_i}{n}$$

Calculate the mean calibration factor for each target analyte (including the SPCCs), as follows:

$$\text{mean CF} = \frac{\sum_{i=1}^n \text{CF}_i}{n}$$

12.4 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the calibration factors for each compound from the initial calibration, as follows:

$$\text{SD} = \sqrt{\frac{\sum_{i=1}^n (\text{CF}_i - \overline{\text{CF}})^2}{n-1}} \qquad \text{RSD} = \frac{\text{SD}}{\overline{\text{CF}}} \times 100$$

where:

$\text{CF}_i$  = CF for each of the calibration standards

$\overline{\text{CF}}$  = Mean CF for each compound from the initial calibration

$n$  = Number of calibration standards, e.g., 5

12.5 Calculate the percent difference (%D) of the calibration factor determined during the calibration verification and the mean calibration factor from the most recent initial calibration, using the equation below:

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

where:

$\overline{CF}$  = Mean CF from the initial calibration

$CF_v$  = CF from the calibration verification standard

12.6 Where appropriate, calculate the percent dry weight of a solid sample using the equation below and the weights determined in Sec. 11.1.2.

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

## 12.7 Qualitative analysis

The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

12.7.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine, where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time, will be accepted as meeting this criterion.

12.7.2 The retention time (RT) of the sample component is within  $\pm 30$  seconds of the RT of the standard component.

12.7.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

12.7.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

12.7.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

12.7.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

12.7.7 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

- (1) Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- (2) The relative intensities of the major ions should agree within  $\pm 20\%$ .  
(Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).
- (3) Molecular ions present in the reference spectrum should be present in the sample spectrum.
- (4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
- (5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

## 12.8 Quantitative analysis

Quantitative of target analytes requires four distinct steps: calculation of the  $\alpha$ -effects on the  $\beta$ -surrogates, calculations of the boiling point effects, calculation of the relative volatility effects on recovery, and finally, recovery correction of the quantity of analyte measured by the mass spectrometer to reflect these three effects. An explanation of these effects and the use of the following equations are given in greater detail in References 5 and 6.



### 12.8.1 Calculation of $\alpha$ -effects on the $\beta$ -surrogates

The initial approximation of the  $\alpha$ -effect on the  $\beta$ -surrogates is accomplished by using the  $\alpha$ -surrogates, fluorobenzene and 1,2-dichloroethane- $d_4$  (boiling points of 85 and 84 °C, respectively), with the assumption that  $\beta$ -effects are minimal at 85 °C. The equation used is:

$$\ln(R_\alpha) = e^{(c_1 \times \alpha_k)} + c_2$$

where:

- $R_\alpha$  = The surrogate's relative recovery corresponding to its  $\alpha_k$ -value  
 $\alpha_k$  = Relative volatility of the surrogate (describes the  $\alpha$ -effect versus recovery relationship).  
 $c_1, c_2$  = Empirically-derived constants

The relative recoveries of the  $\beta$ -surrogates (toluene- $d_8$ , chlorobenzene- $d_5$ , bromobenzene- $d_5$  and 1,2-dichlorobenzene- $d_4$ ) are adjusted for their  $\alpha$ -effects ( $R_\beta$  = measured recovery/ $R_\alpha$ ). The resulting relative recovery represents the component of the relative recovery related to  $\beta$ -effects. Similarly, the  $\alpha$ -surrogates (1,2-dichloroethane- $d_4$  and 1,4-dioxane- $d_8$ ) are used to interpolate  $R_\beta$  for the  $\beta$ -surrogate 1-methylnaphthalene- $d_{10}$ .

### 12.8.2 Calculation of boiling point effects

Using the  $\beta$ -surrogate  $R_\beta$  values, the  $R_\beta$ -boiling point relationship is described using the equation:

$$R_\beta = (c_3 \times [bp - bp_0]) + c_4$$

where:

- $R_\beta$  = The  $\beta$ -surrogate's relative recovery corresponding to the boiling point  
 $bp$  = The analyte's boiling point  
 $bp_0$  = The lowest boiling point of the  $\beta$ -surrogate used in the solution  
 $c_3, c_4$  = Empirically-derived constants

The impact of a single  $\beta$ -surrogate relative-recovery measurement error is minimized by calculating three solutions to the equation above for each analyte. The  $\beta$ -surrogate pairs used to solve this equation for groups of analytes by boiling point are identified in Table 5. The average and standard deviation of the three  $R_\beta$  values (only two solutions for the 80 to 111 °C and 220 to 250 °C ranges) generates the predicted analyte relative recovery range,  $\bar{R}_\beta \pm r_\beta$ , corresponding to  $\beta$ -effects. The resultant  $\bar{R}_\beta$  for each  $\alpha$ -surrogate is used to correct their measured relative responses ( $R_\alpha$  = measured recovery/ $\bar{R}_\beta$ ) to isolate the relative recoveries related to  $\alpha$ -effects.

### 12.8.3 Calculation of the relative volatility effects on recovery

The  $\alpha$ -surrogate corrections are performed by grouping analytes with similar  $\alpha_K$ -values. The  $\alpha$ -effects exhibited by those compounds at the limits of a group are the best data to describe the  $\alpha$ -effects for those analytes within these groups and therefore pairs of  $\alpha$ -surrogates are selected to represent the extremes of each group's range of  $\alpha_K$ -values (i.e., the surrogates hexafluorobenzene and fluorobenzene represent the lower and upper ends of the grouping of  $\alpha$ -values between 0.07 and 3).

One lower-value  $\alpha$ -surrogate and one higher-value  $\alpha$ -surrogate are selected to calculate the relationship of relative recovery to  $\alpha_K$ -values within the group. Using the four possible combinations of surrogates to solve the equation in 12.8.1, each analyte will have four  $\alpha$ -effect measurements. The equation used is:

$$\ln(R_\alpha) = e^{(c_1 \times \alpha_x)} + c_2$$

where:

- $R_\alpha$  = The surrogate's relative recovery corresponding to its  $\alpha_K$ -value
- $\alpha_x$  = Relative volatility of compound X (describes the  $\alpha$ -effect versus recovery relationship).
- $c_1, c_2$  = Empirically-derived constants

12.8.4 The predicted relative recovery relating to  $\alpha$ -effects for an analyte is  $\bar{R}_\alpha \pm r_\alpha$ . The predicted total relative recovery that includes  $\alpha$ - and  $\beta$ -effects is:

$$R_T = \bar{R}_\alpha \times \bar{R}_\beta$$

where:

- $\bar{R}_\alpha$  = Average relative recovery using the equation in 12.8.3.
- $\bar{R}_\beta$  = Average relative recovery using the equation in 12.8.2 for the combinations of  $\beta$ -surrogates in the analytes boiling point grouping.
- $R_T$  = Predicted total relative recovery

The associated variance term is:

$$r_T^2 = r_\alpha^2 + r_\beta^2$$

where the  $r$  values are the standard deviations of the corresponding relative recoveries.

### 12.8.5 Calculation of sample concentration

The calculation of the concentration in a sample is a three-step process.

12.8.5.1 The amount (mass in ng) of the analyte detected by the mass spectrometer is calculated using an external standard approach, such that:

$$\text{Amount (ng)} = \frac{(A_s)(D)}{(\overline{CF})}$$

where:

$A_s$  = Area (or height) of the peak for the analyte in the sample.

$D$  = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made,  $D = 1$ . The dilution factor is always dimensionless.

$\overline{CF}$  = Mean calibration factor from the initial calibration (area per ng).

12.8.5.2 The relative recovery ( $R_T$ ) is predicted from the equations in Secs. 12.8.1 - 12.8.4.

12.8.5.3 The third step is to perform the recovery correction on the amount of analyte detected and to relate that amount to the size of the actual sample, as described below:

$$\text{Concentration} = \frac{(\text{ng analyte detected})}{R_T \times (\text{sample size})}$$

For aqueous samples, the sample size is expressed in mL, leading to a concentration in ng/mL, which is equivalent to  $\mu\text{g/L}$ . For solid samples, oil samples, and tissues, the sample size is expressed in g, leading to a concentration in ng/g, which is equivalent to  $\mu\text{g/kg}$ .

Using the variance term in Sec. 12.8.4, a concentration range can be calculated for each analyte.

## 12.9 Calculation of check surrogate recovery

The check surrogates are used to monitor the overall performance of the analytical system. The recovery of each check surrogate is calculated in a fashion similar to the analyte concentrations, correcting the mass spectrometer response for the recoveries of the other surrogates and the sample size, such that:

$$\text{Recovery} = \frac{(\text{ng check surrogate detected})}{R_T \times (\text{ng of check surrogate spiked})}$$

## 12.10 Reporting matrix corrections

A graphical representation of the effect of the sample matrix on the recovery of the analytes may prove useful in evaluating method performance. Although not required, Figure 2 provides an example of one form of such documentation.

## 13.0 METHOD PERFORMANCE

13.1 The recovery of the target analytes spiked into three soils is summarized in Table 6, along with the relative error of replicate recovery measurements and the precision of the surrogate recoveries in these spiked samples.

13.2 Similar recovery data from an oil sample spiked with the target analytes are presented in Table 7.

13.3 The MDL is defined in Chapter One. **The MDLs for water, soil, oil, and waste oil matrices are presented in Table 8 and are provided for illustrative purposes only.** These MDLs were based on the analysis of 21 replicate samples of each spiked matrix, which is not the same procedure described in either Chapter One or 40 CFR 136. The MDL values presented in Table 8 are corrected for the recoveries of the surrogates. Each laboratory should develop its own matrix-specific MDLs, if necessary, using the guidance found in Chapter One.

13.4 The target analytes were spiked into water containing salt, soap, and glycerine, as a test of the effects of ionic strength, surfactants, etc., on the VD/GC/MS procedure. The recovery data from these analyses are provided in Table 9.

## 14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of a waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St. NW, Washington, D.C. 20036, (202) 872-4477.

14.3 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards that will require disposal.

## 15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges

laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

## 16.0 REFERENCES

1. Hiatt, M.H. "Analysis of Fish and Sediment For Volatile Priority Pollutants," *Analytical Chemistry* 1981, 53 (9), 1541.
2. Hiatt, M.H. "Determination of Volatile Organic Compounds in Fish Samples by Vacuum Distillation and Fused Silica Capillary Gas Chromatography/Mass Spectrometry," *Analytical Chemistry*, 1983, 55 (3), 506.
3. United States Patent 5,411,707, May 2, 1995. "Vacuum Extractor with Cryogenic Concentration and Capillary Interface," assigned to the United States of America, as represented by the Administrator of the Environmental Protection Agency. Washington, DC.
4. Hiatt, Michael H., David R. Youngman and Joseph R. Donnelly, "Separation and Isolation of Volatile Organic Compounds Using Vacuum Distillation with GC/MS Determination," *Analytical Chemistry*, 1994, 66 (6), 905.
5. Hiatt, Michael H. and Carole M. Farr, "Volatile Organic Compound Determination Using Surrogate-Based Correction for Method and Matrix Effects," *Analytical Chemistry*, 1995, 67 (2), 426.
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7. "The Waste Management Manual for Laboratory Personnel," American Chemical Society, Department of Government Regulations and Science Policy, Washington, DC.
8. Hiatt, Michael H., "Analyses of Fish Tissue by Vacuum Distillation/Gas Chromatography/Mass Spectrometry," *Analytical Chemistry*, 1997, 69(6), 1127-1134.
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## 17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 through 11, Figures 1 and 2, a flow diagram of the method procedure, and a glossary of terms specific to this method.

TABLE 1

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA<sup>a</sup>

| m/z | Required Intensity (relative abundance)        |
|-----|--|
| 50  | 15 to 40% of m/z 95                            |
| 75  | 30 to 60% of m/z 95                            |
| 95  | Base peak, 100% relative abundance             |
| 96  | 5 to 9% of m/z 95                              |
| 173 | Less than 2% of m/z 174                        |
| 174 | Greater than 50% of m/z 95                     |
| 175 | 5 to 9% of m/z 174                             |
| 176 | Greater than 95% but less than 101% of m/z 174 |
| 177 | 5 to 9% of m/z 176                             |

<sup>a</sup>Alternative tuning criteria may be used, (e.g. CLP, Method 524.2, or manufacturer's instructions), provided that method performance is not adversely affected.

TABLE 2

## CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANIC COMPOUNDS

| Compound                    | Primary Characteristic Ion | Secondary Characteristic Ion(s) |
|-----------------------------|----------------------------|---------------------------------|
| Acetone                     | 58                         | 43                              |
| Acetonitrile                | 41                         | 41, 40, 39                      |
| Acetophenone                | 105                        | -                               |
| Acrolein                    | 56                         | 55, 58                          |
| Acrylonitrile               | 53                         | 52, 51                          |
| Allyl chloride              | 76                         | 76, 41, 39, 78                  |
| Aniline                     | 66                         | 93                              |
| Benzene                     | 78                         | -                               |
| Bromobenzene                | 156                        | 158                             |
| Bromochloromethane          | 128                        | 49, 130                         |
| Bromodichloromethane        | 83                         | 85, 127                         |
| Bromoform                   | 173                        | 175, 254                        |
| Bromomethane                | 94                         | 96                              |
| 2-Butanone                  | 72                         | 43, 72                          |
| <i>n</i> -Butylbenzene      | 134                        | 91, 92                          |
| <i>sec</i> -Butylbenzene    | 134                        | 105                             |
| <i>tert</i> -Butylbenzene   | 134                        | 91, 119                         |
| Carbon disulfide            | 76                         | 78                              |
| Carbon tetrachloride        | 117                        | 119                             |
| Chlorobenzene               | 112                        | 77, 114                         |
| Chlorodibromomethane        | 129                        | 208, 206                        |
| Chloroethane                | 64                         | 66                              |
| 2-Chloroethyl vinyl ether   | 63                         | 65, 106                         |
| Chloroform                  | 83                         | 85                              |
| Chloromethane               | 50                         | 52                              |
| 2-Chlorotoluene             | 126                        | 91                              |
| 4-Chlorotoluene             | 126                        | 91                              |
| 1,2-Dibromo-3-chloropropane | 157                        | 75, 155                         |
| Dibromomethane              | 174                        | 93, 95                          |
| 1,2-Dibromomethane          | 107                        | 109                             |
| 1,2-Dichlorobenzene         | 146                        | 111, 148                        |
| 1,3-Dichlorobenzene         | 146                        | 111, 148                        |

TABLE 2  
(continued)

| Compound                            | Primary Characteristic Ion | Secondary Characteristic Ion(s) |
|-------------------------------------|----------------------------|---------------------------------|
| 1,4-Dichlorobenzene                 | 146                        | 111, 148                        |
| <i>cis</i> -1,4-Dichloro-2-butene   | 75                         | 75, 53, 77, 124, 89             |
| <i>trans</i> -1,4-Dichloro-2-butene | 53                         | 88, 75                          |
| Dichlorodifluoromethane             | 85                         | 87                              |
| 1,1-Dichloroethane                  | 63                         | 65, 83                          |
| 1,2-Dichloroethane                  | 62                         | 98                              |
| 1,1-Dichloroethene                  | 96                         | 61, 63                          |
| <i>cis</i> -1,2-Dichloroethene      | 96                         | 61, 98                          |
| <i>trans</i> -1,2-Dichloroethene    | 96                         | 61, 98                          |
| 1,2-Dichloropropane                 | 63                         | 112                             |
| 1,3-Dichloropropane                 | 76                         | 78                              |
| 2,2-Dichloropropane                 | 77                         | 97                              |
| 1,1-Dichloropropene                 | 75                         | 110, 77                         |
| <i>cis</i> -1,3-Dichloropropene     | 75                         | 77, 39                          |
| <i>trans</i> -1,3-Dichloropropene   | 75                         | 77, 39                          |
| Diethyl ether                       | 74                         | 45, 59                          |
| 1,4-Dioxane                         | 88                         | 88, 58, 43, 57                  |
| Ethyl acetate                       | 88                         | 43, 45, 61                      |
| Ethylbenzene                        | 91                         | 106                             |
| Ethyl methacrylate                  | 69                         | 69, 41, 99, 86, 114             |
| Hexachlorobutadiene                 | 225                        | 223, 227                        |
| 2-Hexanone                          | 58                         | 100                             |
| Iodomethane                         | 142                        | 127, 141                        |
| Isobutyl alcohol                    | 74                         | 43, 41, 42                      |
| Isopropylbenzene                    | 120                        | 105                             |
| <i>p</i> -Isopropyltoluene          | 134                        | 91, 119                         |
| Methacrylonitrile                   | 67                         | 41, 39, 52, 66                  |
| Methylene chloride                  | 84                         | 86, 49                          |
| Methyl methacrylate                 | 69                         | 69, 41, 100, 39                 |
| 1-Methylnaphthalene                 | 142                        | 141                             |
| 2-Methylnaphthalene                 | 142                        | 141                             |
| 4-Methyl-2-pentanone                | 100                        | 43, 58, 85                      |
| Naphthalene                         | 128                        | 127                             |



TABLE 2  
(continued)

| Compound                                   | Primary Characteristic Ion | Secondary Characteristic Ion(s) |
|--|----------------------------|---------------------------------|
| Nitrobenzene                               | 123                        | -                               |
| <i>N</i> -Nitrosodibutylamine              | 84                         | 158                             |
| <i>N</i> -Nitrosodiethylamine              | 102                        | 57                              |
| <i>N</i> -Nitrosodimethylamine             | 74                         | 42                              |
| <i>N</i> -Nitrosodi- <i>n</i> -propylamine | 130                        | 70                              |
| <i>N</i> -Nitrosomethylethylamine          | 88                         | 56, 42                          |
| Pentachloroethane                          | 167                        | 167, 130, 132, 165, 169         |
| 2-Picoline                                 | 93                         | 93, 66, 92, 78                  |
| Propionitrile                              | 54                         | 54, 52, 55, 40                  |
| <i>n</i> -Propylbenzene                    | 120                        | 91                              |
| Pyridine                                   | 79                         | 52                              |
| Styrene                                    | 104                        | 78                              |
| 1,2,3-Trichlorobenzene                     | 180                        | 182, 145                        |
| 1,2,4-Trichlorobenzene                     | 180                        | 182, 145                        |
| 1,1,1,2-Tetrachloroethane                  | 131                        | 133                             |
| 1,1,2,2-Tetrachloroethane                  | 83                         | 131, 85                         |
| Tetrachloroethene                          | 166                        | 129, 131, 164                   |
| Toluene                                    | 92                         | 91                              |
| <i>o</i> -Toluidine                        | 106                        | 107                             |
| 1,2,3-Trichlorobenzene                     | 180                        | 182                             |
| 1,2,4,-Trichlorobenzene                    | 180                        | 182                             |
| 1,1,1-Trichloroethane                      | 97                         | 99, 61                          |
| 1,1,2-Trichloroethane                      | 97                         | 83, 85                          |
| Trichloroethene                            | 130                        | 95, 97, 132                     |
| Trichlorofluoromethane                     | 101                        | 151, 153                        |
| 1,2,3-Trichloropropane                     | 110                        | 75, 77                          |
| 1,2,4-Trimethylbenzene                     | 120                        | 105                             |
| 1,3,5-Trimethylbenzene                     | 120                        | 105                             |
| Vinyl chloride                             | 62                         | 64                              |
| <i>o</i> -Xylene                           | 106                        | 91                              |
| <i>m</i> -Xylene                           | 106                        | 91                              |
| <i>p</i> -Xylene                           | 106                        | 91                              |

TABLE 2  
(continued)

| Compound                      | Primary Characteristic Ion | Secondary Characteristic Ion(s) |
|-------------------------------|----------------------------|---------------------------------|
| Surrogates                    |                            |                                 |
| Acetone- $d_6$                | 64                         | 46                              |
| Acetophenone- $d_5$           | 110                        | 82                              |
| Benzene- $d_6$                | 84                         | 83                              |
| Bromobenzene- $d_5$           | 82                         | 162                             |
| 4-Bromofluorobenzene          | 174                        | 95, 176                         |
| Chlorobenzene- $d_5$          | 117                        | 119                             |
| Decafluorobiphenyl            | 256                        | 234                             |
| 1,2-Dibromomethane- $d_4$     | 111                        | 113                             |
| 1,2-Dichlorobenzene- $d_4$    | 152                        | 115, 150                        |
| Dichloroethane- $d_4$         | 65                         | 102                             |
| 1,2-Dichloropropane- $d_6$    | 67                         | 69                              |
| Diethyl ether- $d_{10}$       | 84                         | 66, 50                          |
| 1,4-Difluorobenzene           | 114                        | 63                              |
| 1,4-Dioxane- $d_8$            | 96                         | 64                              |
| Ethyl acetate- $^{13}C_2$     | 71                         | 62                              |
| Fluorobenzene                 | 96                         | 77                              |
| Hexafluorobenzene             | 186                        | 117                             |
| Methylene chloride- $d_2$     | 88                         | 90                              |
| Methylnaphthalene- $d_{10}$   | 152                        | 150                             |
| Naphthalene- $d_8$            | 136                        | 108                             |
| Nitrobenzene- $d_5$           | 128                        | 82                              |
| Nitromethane- $d_3$           | 64                         | 46                              |
| Pentafluorobenzene            | 168                        | -                               |
| Pyridine- $d_5$               | 84                         | 56                              |
| Tetrahydrofuran- $d_8$        | 78                         | 80                              |
| 1,2,4-Trichlorobenzene- $d_3$ | 183                        | 185                             |
| 1,1,2-Trichloroethane- $d_3$  | 100                        | -                               |
| Toluene- $d_8$                | 98                         | -                               |
| <i>o</i> -Xylene- $d_{10}$    | 98                         | 116                             |

TABLE 2  
(continued)

The ions listed above are those recommended, but not required, for use in this method. In general, the ions listed as the primary characteristic ion provide a better response or suffer from fewer interferences. However, either the primary ion or one of the secondary ions listed here may be used for quantitation of the analytes, provided that the same ions are used for both calibrations and sample analyses. In some instances, sample-specific interferences may occur that complicate the use of the characteristic ion that was used for the calibration. If such interferences occur, the use of a secondary ion for quantitation must be clearly documented and supported by multi-point calibration factors derived from the same ion.

TABLE 3  
RELATIVE VOLATILITY VALUES ( $\alpha_k$ )

| Compound                                 | Surrogate<br>Type <sup>a</sup> | b.p. <sup>b</sup><br>(°C) | Conc. <sup>c</sup><br>(ppb) | K <sup>d</sup> | α <sub>k</sub> -value |                 |
|--|--------------------------------|---------------------------|-----------------------------|----------------|-----------------------|-----------------|
|  |                                |                           |                             |                | Avg. <sup>e</sup>     | SD <sup>f</sup> |
| <i>Permanent gases (Class I)</i>         |                                |                           |                             |                |                       |                 |
| Dichlorodifluoromethane                  |                                | -30                       | 80                          |                | 0.07                  | 0.02            |
| Trichlorofluoromethane                   |                                | 24                        | 80                          |                | 0.20                  | 0.02            |
| Vinyl chloride                           |                                | -13                       | 80                          |                | 0.48                  | 0.06            |
| Chloroethane                             |                                | 12                        | 80                          |                | 1.01                  | 0.02            |
| Chloromethane                            |                                | -24                       | 80                          |                | 1.37                  | 0.07            |
| Bromomethane                             |                                | 4                         | 80                          |                | 1.82                  | 0.12            |
| <i>Volatiles (Class I)</i>               |                                |                           |                             |                |                       |                 |
| 1,1-Dichloroethene                       |                                | 37                        | 40                          |                | 0.63                  | 0.07            |
| Carbon tetrachloride                     |                                | 76                        | 40                          |                | 0.64                  | 0.02            |
| Hexafluorobenzene                        | α                              | 82                        | 25                          |                | 0.86                  | 0.06            |
| 1,1-Dichloropropene                      |                                | 104                       | 40                          |                | 0.88                  | 0.03            |
| 1,1,1-Trichloroethane                    |                                | 74                        | 40                          | 1.41           | 1.31                  | 0.04            |
| Allyl chloride                           |                                | 45                        | 100                         |                | 1.34                  | 0.45            |
| 2,2-Dichloropropane                      |                                | 69                        | 40                          |                | 1.37                  | 0.18            |
| Tetrachloroethene                        |                                | 121                       | 40                          | 1.55           | 1.43                  | 0.03            |
| Pentafluorobenzene                       | α                              | 85                        | 9                           |                | 1.51                  | 0.04            |
| Iodomethane                              |                                | 42                        | 100                         |                | 2.29                  | 0.43            |
| <i>trans</i> -1,2-Dichloroethene         |                                | 48                        | 40                          |                | 2.3                   | 0.46            |
| Trichloroethene                          |                                | 87                        | 40                          |                | 2.34                  | 0.09            |
| Isopropylbenzene                         |                                | 152                       | 40                          | 2.20           | 2.75                  | 0.05            |
| Fluorobenzene                            | α                              | 85                        | 9                           |                | 3.5                   | 0.21            |
| Benzene                                  |                                | 80                        | 40                          | 4.36           | 3.55                  | 0.27            |
| Ethylbenzene                             |                                | 136                       | 40                          | 3.28           | 3.6                   | 0.12            |
| 1,4-Difluorobenzene                      | α                              | 88                        | 9                           |                | 3.83                  | 0.07            |
| Toluene                                  |                                | 111                       | 40                          | 3.93           | 3.88                  | 0.12            |
| <i>m+p</i> -Xylenes                      |                                | 138                       | 40                          |                | 3.91                  | 0.11            |
| Benzene- <i>d</i> <sub>6</sub>           | c                              | 79                        | 26                          | 4.4            | 3.92                  | 0.27            |
| 1,1-Dichloroethane                       |                                | 57                        | 40                          |                | 4.12                  | 0.08            |
| Toluene- <i>d</i> <sub>8</sub>           | β                              | 111                       | 25                          |                | 4.28                  | 0.09            |
| <i>n</i> -Propylbenzene                  |                                | 159                       | 40                          | 2.49           | 2.43                  | 0.04            |
| <i>cis</i> -1,2-Dichloroethene           |                                | 60                        | 40                          |                | 5.34                  | 0.07            |
| <i>o</i> -Xylene                         |                                | 144                       | 40                          | 5.11           | 5.54                  | 0.09            |
| <i>o</i> -Xylene- <i>d</i> <sub>10</sub> | α                              | 143                       | 25                          | 5.1            | 6.14                  | 0.2             |
| Chlorobenzene- <i>d</i> <sub>5</sub>     | α + β                          | 131                       | 25                          |                | 6.27                  | 0.17            |

TABLE 3  
(continued)

| Compound                                     | Surrogate<br>Type <sup>a</sup> | b.p. <sup>b</sup><br>(°C) | Conc. <sup>c</sup><br>(ppb) | K <sup>d</sup> | α <sub>k</sub> -value |                 |
|--|--------------------------------|---------------------------|-----------------------------|----------------|-----------------------|-----------------|
|  |                                |                           |                             |                | Avg. <sup>e</sup>     | SD <sup>f</sup> |
| <i>Volatiles (continued)</i>                 |                                |                           |                             |                |                       |                 |
| Chloroform                                   |                                | 62                        | 40                          | 5.85           | 6.39                  | 0.09            |
| Styrene                                      |                                | 145                       | 40                          |                | 6.87                  | 0.36            |
| Chlorobenzene                                |                                | 132                       | 40                          |                | 6.07                  | 0.24            |
| Bromobenzene                                 |                                | 156                       | 40                          |                | 7.89                  | 0.73            |
| Bromobenzene- <i>d</i> <sub>5</sub>          | β                              | 155                       | 25                          |                | 7.93                  | 0.59            |
| 4-Bromo-1-fluorobenzene                      | c                              | 152                       | 25                          |                | 8.05                  | 0.7             |
| Methylene chloride                           |                                | 40                        | 40                          | 9.33           | 10.1                  | 1.6             |
| Methylene chloride- <i>d</i> <sub>2</sub>    | c                              | 40                        | 24                          |                | 11.1                  | 1.9             |
| 1,2-Dichloropropane                          |                                | 96                        | 40                          |                | 10.9                  | 0.2             |
| 1,2-Dichloropropane- <i>d</i> <sub>6</sub>   | c                              | 95                        | 21                          |                | 11                    | 0.1             |
| 1,1,1,2-Tetrachloroethane                    |                                | 130                       | 40                          |                | 11.6                  | 0.6             |
| Bromodichloromethane                         |                                | 90                        | 40                          |                | 12.3                  | 0.6             |
| <i>trans</i> -1,3-Dichloropropene            |                                | 112                       | 40                          |                | 14.1                  | 0.7             |
| Bromochloromethane                           |                                | 68                        | 40                          |                | 15.4                  | 0.4             |
| 1,2-Dichloroethane                           |                                | 84                        | 40                          | 20.23          | 18.7                  | 0.9             |
| Dibromochloromethane                         |                                | 120                       | 40                          |                | 19.2                  | 1.4             |
| <i>cis</i> -1,3-Dichloropropene              |                                | 104                       | 40                          |                | 19.6                  | 1.4             |
| 1,2-Dichloroethane- <i>d</i> <sub>4</sub>    | α                              | 84                        | 25                          |                | 20.0                  | 20.0            |
| Bromoform                                    |                                | 150                       | 40                          |                | 23.4                  | 2.4             |
| Dibromomethane                               |                                | 97                        | 40                          |                | 23.9                  | 1.7             |
| 1,3-Dichloropropane                          |                                | 120                       | 40                          |                | 24.9                  | 1.9             |
| 1,2-Dibromoethane- <i>d</i> <sub>4</sub>     | α                              | 131                       | 26                          |                | 26.0                  | 1.7             |
| 1,1,2-Trichloroethane                        |                                | 114                       | 40                          |                | 26.2                  | 2.4             |
| 1,1,2-Trichloroethane- <i>d</i> <sub>3</sub> | c                              | 112                       | 20                          |                | 26.6                  | 0.7             |
| 1,2-Dibromoethane                            |                                | 132                       | 40                          |                | 26.7                  | 2.0             |
| 1,1,2,2-Tetrachloroethane                    |                                | 146                       | 40                          |                | 30.3                  | 2.8             |
| <i>cis</i> -1,4-Dichloro-2-butene            |                                | 152                       | 100                         |                | 33.3                  | 8.1             |
| 1,2,3-Trichloropropane                       |                                | 157                       | 40                          |                | 33.6                  | 2.9             |
| <i>trans</i> -1,4-Dichloro-2-butene          |                                | 156                       | 100                         |                | 33.8                  | 7.4             |
| <i>Neutral semivolatiles (Class II)</i>      |                                |                           |                             |                |                       |                 |
| <i>n</i> -Butylbenzene                       |                                | 183                       | 40                          | 1.65           | 1.88                  | 0.08            |
| <i>sec</i> -Butylbenzene                     |                                | 173                       | 40                          |                | 1.91                  | 0.04            |
| Hexachlorobutadiene                          |                                | 215                       | 40                          |                | 2.08                  | 0.06            |
| <i>p</i> -Isopropyltoluene                   |                                | 183                       | 40                          | 2.25           | 2.5                   | 0.07            |
| <i>tert</i> -Butylbenzene                    |                                | 169                       | 40                          |                | 2.72                  | 0.05            |

TABLE 3  
(continued)

| Compound                                      | Surrogate<br>Type <sup>a</sup> | b.p. <sup>b</sup><br>(°C) | Conc. <sup>c</sup><br>(ppb) | K <sup>d</sup> | α <sub>k</sub> -value |                 |
|---|--------------------------------|---------------------------|-----------------------------|----------------|-----------------------|-----------------|
|   |                                |                           |                             |                | Avg. <sup>e</sup>     | SD <sup>f</sup> |
| <i>Neutral semivolatiles (continued)</i>      |                                |                           |                             |                |                       |                 |
| Decafluorobiphenyl                            | β                              | 206                       | 25                          | 3.52           | 3.03                  | 0.06            |
| 1,3,5-Trimethylbenzene                        |                                | 165                       | 40                          |                | 3.75                  | 0.18            |
| 2-Chlorotoluene                               |                                | 159                       | 40                          |                | 4.04                  | 0.17            |
| 1,2,4-Trimethylbenzene                        |                                | 169                       | 40                          |                | 4.5                   | 0.4             |
| 4-Chlorotoluene                               |                                | 162                       | 40                          |                | 4.78                  | 0.43            |
| 1,3-Dichlorobenzene                           |                                | 173                       | 40                          |                | 5.72                  | 0.73            |
| 1,4-Dichlorobenzene                           |                                | 174                       | 40                          |                | 6.14                  | 0.84            |
| 1,2,4-Trichlorobenzene                        |                                | 214                       | 40                          |                | 7.73                  | 1.22            |
| 1,2-Dichlorobenzene                           |                                | 180                       | 40                          |                | 7.86                  | 1.19            |
| 1,2,4-Trichlorobenzene- <i>d</i> <sub>3</sub> | β                              | 213                       | 25                          |                | 7.88                  | 1.19            |
| 1,2-Dichlorobenzene- <i>d</i> <sub>4</sub>    | β                              | 181                       | 24                          | 8.03           | 1.23                  |                 |
| 1,2,3-Trichlorobenzene                        |                                | 218                       | 40                          |                | 11.3                  | 1.6             |
| Pentachloroethane                             |                                | 162                       | 100                         |                | 13.2                  | 3.3             |
| Naphthalene                                   |                                | 218                       | 40                          |                | 16.7                  | 2.2             |
| Naphthalene- <i>d</i> <sub>8</sub>            | c                              | 217                       | 25                          |                | 18                    | 3.7             |
| 1,2-Dibromo-3-chloropropane                   |                                | 196                       | 40                          |                | 38.9                  | 4.9             |
| 1-Methylnaphthalene- <i>d</i> <sub>10</sub>   | β                              | 241                       | 100                         |                |                       | 67              |
| 2-Methylnaphthalene                           |                                | 245                       | 500                         |                | 67                    | 17              |
| <i>Soluble volatiles (Class III)</i>          |                                |                           |                             |                |                       |                 |
| Diethyl ether                                 |                                | 35                        | 80                          |                | 34.9                  | 5.7             |
| Ethyl methacrylate                            |                                | 117                       | 100                         |                | 48.4                  | 2.8             |
| Methyl methacrylate                           |                                | 101                       | 100                         |                | 71.4                  | 4.1             |
| Methacrylonitrile                             |                                | 90                        | 100                         |                | 102.9                 | 2.4             |
| Acrolein                                      |                                | 53                        | 200                         | 180            | 116.8                 | 1               |
| 4-Methyl-2-pentanone                          |                                | 117                       | 100                         |                | 119.9                 | 8.4             |
| 2-Hexanone                                    |                                | 128                       | 100                         |                | 131.1                 | 2.1             |
| Ethyl acetate- <sup>13</sup> C <sub>2</sub>   | α                              | 77                        | 250                         | 150            |                       | 150             |
| Acrylonitrile                                 |                                | 78                        | 100                         |                | 161                   | 32.0            |
| Acetophenone- <i>d</i> <sub>5</sub>           | c                              | 202                       | 100                         |                | 161                   | 20.0            |
| Isobutyl alcohol                              |                                | 108                       | 100                         |                | 1750                  | 156.0           |
| Tetrahydrofuran                               |                                | 66                        | N/A                         |                | 456                   | 67.0            |
| Acetonitrile                                  |                                | 82                        | 100                         | 1200           | 545                   | 103.0           |
| Acetone                                       |                                | 56                        | 100                         | 580            | 600                   | 32.0            |
| Acetone- <i>d</i> <sub>6</sub>                | α                              | 57                        | 490                         | 600            | 600                   |                 |
| 2-Butanone                                    |                                | 80                        | 100                         | 380            | 770                   | 110             |

TABLE 3  
(continued)

| Compound                                   | Surrogate<br>Type <sup>a</sup> | b.p. <sup>b</sup><br>(°C) | Conc. <sup>c</sup><br>(ppb) | K <sup>d</sup> | α <sub>k</sub> -value |                 |
|--|--------------------------------|---------------------------|-----------------------------|----------------|-----------------------|-----------------|
|  |                                |                           |                             |                | Avg. <sup>e</sup>     | SD <sup>f</sup> |
| <i>Soluble volatiles (continued)</i>       |                                |                           |                             |                |                       |                 |
| Propionitrile                              |                                | 97                        | 100                         |                | 1420                  | 320             |
| 1,4-Dioxane- <i>d</i> <sub>8</sub>         | α                              | 101                       | 240                         | 5800           | 5800                  |                 |
| 1,4-Dioxane                                |                                | 101                       | 100                         | 5750           | 6200                  | 700             |
| 2-Picoline                                 |                                | 129                       | 100                         |                | 6800                  | 5200            |
| Pyridine                                   |                                | 116                       | 100                         |                | 13100                 | 600             |
| Pyridine- <i>d</i> <sub>5</sub>            | α                              | 115                       | 100                         | 15000          | 15000                 |                 |
| <i>Basic semivolatiles (Class IV)</i>      |                                |                           |                             |                |                       |                 |
| <i>N</i> -Nitrosodimethylamine             |                                | 154                       | 500                         |                | 129                   | 37.3            |
| <i>N</i> -Nitrosomethylethylamine          |                                | 165                       | 500                         |                | 1900                  | 800             |
| <i>N</i> -Nitrosodi- <i>n</i> -propylamine |                                | 206                       | 500                         |                | 2400                  | 2000            |
| <i>N</i> -Nitrosodiethylamine              |                                | 177                       | 500                         |                | 4900                  | 2200            |
| Aniline                                    |                                | 184                       | 500                         |                | 13700                 | 2300            |
| <i>o</i> -Toluidine                        |                                | 200                       | 500                         |                | 15200                 | 2100            |
| <i>N</i> -Nitrosodibutylamine              |                                | 240                       | 500                         |                | 21000                 | 5000            |

<sup>a</sup>Surrogate Type:  $\alpha$  =  $\alpha$ -surrogate  
 $\beta$  =  $\beta$ -surrogate  
c = check surrogate

<sup>b</sup>Boiling point of analyte

<sup>c</sup>Concentration of analyte in solutions used to determine  $\alpha$ -values

<sup>d</sup>Partition coefficient of analyte between headspace and water at 20 °C

<sup>e</sup>Average of 3 to 4 replicates

<sup>f</sup>One standard deviation

TABLE 4

RELATIVE VOLATILITY RANGES OF THE GAS-LIQUID PARTITIONING ( $\alpha$ -) SURROGATES

| Relative Volatility Range | Surrogate Pairs            |                            |
|---------------------------|----------------------------|----------------------------|
| 0.07 to 3.0               | Hexafluorobenzene          | Fluorobenzene              |
|                           | Hexafluorobenzene          | 1,4-Difluorobenzene        |
|                           | Pentafluorobenzene         | Fluorobenzene              |
|                           | Pentafluorobenzene         | 1,4-Difluorobenzene        |
| 3.0 to 6.3                | Fluorobenzene              | <i>o</i> -Xylene- $d_{10}$ |
|                           | Fluorobenzene              | Chlorobenzene- $d_5$       |
|                           | 1,4-Difluorobenzene        | <i>o</i> -Xylene- $d_{10}$ |
|                           | 1,4-Difluorobenzene        | Chlorobenzene- $d_5$       |
| 6.3 to 20                 | <i>o</i> -Xylene- $d_{10}$ | 1,2-Dichloroethane- $d_4$  |
|                           | <i>o</i> -Xylene- $d_{10}$ | 1,2-Dibromoethane- $d_4$   |
|                           | Chlorobenzene- $d_5$       | 1,2-Dichloroethane- $d_4$  |
|                           | Chlorobenzene- $d_5$       | 1,2-Dibromoethane- $d_4$   |
| 20 to 600                 | 1,2-Dichloroethane- $d_4$  | Tetrahydrofuran- $d_8$     |
|                           | 1,2-Dichloroethane- $d_4$  | 1,4-Dioxane- $d_8$         |
|                           | 1,2-Dibromoethane- $d_4$   | Tetrahydrofuran- $d_8$     |
|                           | 1,2-Dibromoethane- $d_4$   | 1,4-Dioxane- $d_8$         |
| 600 to 6000               | Tetrahydrofuran- $d_8$     | 1,4-Dioxane- $d_8$         |
|                           | Nitromethane- $d_3$        | 1,4-Dioxane- $d_8$         |



TABLE 5

BOILING POINT RANGES OF THE BOILING POINT ( $\beta$ -) SURROGATES

| Boiling Point Range ( $^{\circ}\text{C}$ ) | Surrogate Pairs            |                               |
|--|----------------------------|-------------------------------|
| 80 to 111                                  | Toluene- $d_8$             | 80 $^{\circ}\text{C}^a$       |
|  | Chlorobenzene- $d_5$       | 80 $^{\circ}\text{C}^a$       |
| 111 to 131                                 | Toluene- $d_8$             | Chlorobenzene- $d_5$          |
|  | Toluene- $d_8$             | Bromobenzene- $d_5$           |
|  | Chlorobenzene- $d_5$       | 80 $^{\circ}\text{C}^a$       |
| 131 to 155                                 | Toluene- $d_8$             | Bromobenzene- $d_5$           |
|  | Chlorobenzene- $d_5$       | Bromobenzene- $d_5$           |
|  | Chlorobenzene- $d_5$       | 1,2-Dichlorobenzene- $d_4$    |
| 155 to 181                                 | Chlorobenzene- $d_5$       | 1,2-Dichlorobenzene- $d_4$    |
|  | Bromobenzene- $d_5$        | 1,2-Dichlorobenzene- $d_4$    |
|  | Bromobenzene- $d_5$        | Decafluorobiphenyl            |
| 181 to 206                                 | Bromobenzene- $d_5$        | Decafluorobiphenyl            |
|  | 1,2-Dichlorobenzene- $d_4$ | Decafluorobiphenyl            |
|  | 1,2-Dichlorobenzene- $d_4$ | 1,2,4-Trichlorobenzene- $d_3$ |
| 206 to 220                                 | 1,2-Dichlorobenzene- $d_4$ | 1,2,4-Trichlorobenzene- $d_3$ |
|  | Decafluorobiphenyl         | 1,2,4-Trichlorobenzene- $d_3$ |
|  | Decafluorobiphenyl         | 1-Methylnaphthalene- $d_{10}$ |
| 220 to 250                                 | Decafluorobiphenyl         | 1-Methylnaphthalene- $d_{10}$ |
|  | Decafluorobiphenyl         | 1-Methylnaphthalene- $d_{10}$ |

<sup>a</sup> The boiling point effects relating to an analyte with a boiling point of  $\leq 80^{\circ}\text{C}$  are assumed to be negligible.

TABLE 6

RECOVERY OF ANALYTES SPIKED INTO THREE SOILS  
AND ANALYZED BY VACUUM DISTILLATION GC/MS

| Compound                                   | Soil #1 <sup>a</sup> |                        |                      | Soil #2 <sup>b</sup> |                        |                      | Soil #3 <sup>c</sup> |                        |                      |
|--|----------------------|------------------------|----------------------|----------------------|------------------------|----------------------|----------------------|------------------------|----------------------|
|  | % Rec <sup>d</sup>   | Rel Error <sup>e</sup> | Sur Pre <sup>f</sup> | % Rec <sup>d</sup>   | Rel Error <sup>e</sup> | Sur Pre <sup>f</sup> | % Rec <sup>d</sup>   | Rel Error <sup>e</sup> | Sur Pre <sup>f</sup> |
| Dichlorodifluoromethane                    | 128                  | 28                     | 0                    | 122                  | 30                     | 92                   | 22                   | 4                      | 4                    |
| Chloromethane                              | 116                  | 9                      | 0                    | 109                  | 13                     | 74                   | 71                   | 6                      | 12                   |
| Vinyl chloride                             | 114                  | 14                     | 0                    | 118                  | 18                     | 87                   | 94                   | 7                      | 15                   |
| Bromomethane                               | 106                  | 12                     | 0                    | 101                  | 12                     | 62                   | 24                   | 1                      | 2                    |
| Chloroethane                               | 109                  | 11                     | 0                    | 110                  | 11                     | 75                   | 15                   | 0                      | 2                    |
| Trichlorofluoromethane                     | 111                  | 11                     | 0                    | 125                  | 14                     | 98                   | 12                   | 0                      | 2                    |
| Diethyl ether                              | 20                   | 8                      | 1                    | 18                   | 8                      | 6                    | 10                   | 1                      | 1                    |
| Acetone                                    | 112                  | 3                      | 6                    | 102                  | 4                      | 75                   | 139                  | 21                     | 60                   |
| 1,1-Dichloroethene                         | 110                  | 4                      | 0                    | 120                  | 17                     | 91                   | 68                   | 7                      | 10                   |
| Iodomethane                                | 106                  | 6                      | 0                    | 96                   | 15                     | 56                   | 94                   | 3                      | 6                    |
| Allyl chloride                             | 116                  | 8                      | 0                    | 111                  | 12                     | 77                   | 88                   | 4                      | 10                   |
| Methylene chloride- <i>d</i> <sub>6</sub>  | 105                  | 6                      | 2                    | 96                   | 6                      | 60                   | 101                  | 3                      | 2                    |
| Methylene chloride                         | 104                  | 5                      | 2                    | 94                   | 4                      | 57                   | 94                   | 4                      | 2                    |
| Acrylonitrile                              | 106                  | 5                      | 7                    | 93                   | 4                      | 60                   | 135                  | 9                      | 62                   |
| <i>trans</i> -1,2-Dichloroethene           | 99                   | 8                      | 0                    | 93                   | 9                      | 53                   | 85                   | 5                      | 6                    |
| 1,1-Dichloroethane                         | 109                  | 5                      | 1                    | 103                  | 2                      | 66                   | 179                  | 0                      | 0                    |
| Methacrylonitrile                          | 106                  | 3                      | 6                    | 69                   | 7                      | 35                   | 152                  | 2                      | 11                   |
| 2-Butanone                                 | 112                  | 11                     | 6                    | 102                  | 4                      | 77                   | 152                  | 9                      | 64                   |
| Propionitrile                              | 122                  | 4                      | 6                    | 109                  | 2                      | 83                   | 167                  | 6                      | 64                   |
| 2,2-Dichloropropane                        | 105                  | 1                      | 0                    | 115                  | 7                      | 83                   | 89                   | 1                      | 10                   |
| <i>cis</i> -1,2-Dichloroethene             | 101                  | 2                      | 2                    | 97                   | 0                      | 59                   | 101                  | 1                      | 2                    |
| Chloroform                                 | 99                   | 2                      | 3                    | 98                   | 2                      | 62                   | 103                  | 0                      | 2                    |
| Isobutyl alcohol                           | 103                  | 9                      | 6                    | 105                  | 6                      | 75                   | NA                   | NA                     | NA                   |
| Bromochloromethane                         | 98                   | 0                      | 2                    | 93                   | 2                      | 59                   | 105                  | 1                      | 2                    |
| 1,1,1-Trichloroethane                      | 99                   | 1                      | 0                    | 112                  | 6                      | 78                   | 85                   | 1                      | 10                   |
| 1,1-Dichloropropene                        | 102                  | 2                      | 2                    | 120                  | 7                      | 87                   | 83                   | 1                      | 12                   |
| Carbon tetrachloride                       | 93                   | 3                      | 0                    | 112                  | 8                      | 78                   | 83                   | 1                      | 12                   |
| Benzene- <i>d</i> <sub>6</sub>             | 102                  | 1                      | 1                    | 99                   | 1                      | 60                   | 102                  | 1                      | 1                    |
| 1,2-Dichloroethane                         | 99                   | 1                      | 2                    | 94                   | 0                      | 108                  | 108                  | 1                      | 3                    |
| Benzene                                    | 101                  | 1                      | 1                    | 98                   | 1                      | 101                  | 101                  | 1                      | 1                    |
| Trichloroethene                            | 90                   | 2                      | 1                    | 94                   | 1                      | 95                   | 95                   | 2                      | 6                    |
| 1,2-Dichloropropane- <i>d</i> <sub>6</sub> | 102                  | 1                      | 2                    | 101                  | 1                      | 103                  | 103                  | 1                      | 2                    |
| 1,2-Dichloropropane                        | 102                  | 2                      | 3                    | 101                  | 1                      | 102                  | 102                  | 1                      | 2                    |
| Methyl methacrylate                        | 152                  | 2                      | 9                    | 149                  | 11                     | 145                  | 145                  | 4                      | 13                   |
| Bromodichloromethane                       | 94                   | 2                      | 2                    | 95                   | 1                      | 103                  | 103                  | 1                      | 2                    |
| 1,4-Dioxane                                | 110                  | 1                      | 5                    | 103                  | 1                      | 123                  | 123                  | 2                      | 29                   |

TABLE 6  
(continued)

| Compound                                     | Soil #1 <sup>a</sup> |                        |                      | Soil #2 <sup>b</sup> |                        |                      | Soil #3 <sup>c</sup> |                        |                      |
|--|----------------------|------------------------|----------------------|----------------------|------------------------|----------------------|----------------------|------------------------|----------------------|
|  | % Rec <sup>d</sup>   | Rel Error <sup>e</sup> | Sur Pre <sup>f</sup> | % Rec <sup>d</sup>   | Rel Error <sup>e</sup> | Sur Pre <sup>f</sup> | % Rec <sup>d</sup>   | Rel Error <sup>e</sup> | Sur Pre <sup>f</sup> |
| Dibromomethane                               | 93                   | 2                      | 5                    | 93                   | 1                      | 105                  | 105                  | 1                      | 9                    |
| 4-Methyl-2-pentanone                         | 125                  | 2                      | 8                    | 112                  | 6                      | 147                  | 147                  | 4                      | 13                   |
| <i>trans</i> -1,3-Dichloropropene            | 99                   | 1                      | 3                    | 99                   | 0                      | 101                  | 101                  | 1                      | 2                    |
| Toluene                                      | 99                   | 0                      | 3                    | 99                   | 1                      | 96                   | 96                   | 1                      | 1                    |
| Pyridine                                     | 95                   | 5                      | 8                    | 119                  | 1                      | 71                   | 71                   | 3                      | 43                   |
| <i>cis</i> -1,3-Dichloropropene              | 91                   | 2                      | 2                    | 93                   | 1                      | 102                  | 102                  | 1                      | 3                    |
| <i>N</i> -Nitrosodimethylamine               | 68                   | 5                      | 4                    | 54                   | 11                     | 20                   | 20                   | 1                      | 2                    |
| 1,1,2-Trichloroethane- <i>d</i> <sub>3</sub> | 95                   | 3                      | 5                    | 100                  | 4                      | 102                  | 102                  | 1                      | 8                    |
| 2-Hexanone                                   | 125                  | 6                      | 6                    | 110                  | 4                      | 145                  | 145                  | 8                      | 13                   |
| 1,1,2-Trichloroethane                        | 93                   | 2                      | 5                    | 96                   | 2                      | 103                  | 103                  | 1                      | 9                    |
| Tetrachloroethene                            | 98                   | 7                      | 2                    | 105                  | 2                      | 123                  | 123                  | 8                      | 14                   |
| 1,3-Dichloropropane                          | 99                   | 1                      | 6                    | 101                  | 1                      | 103                  | 103                  | 1                      | 9                    |
| Dibromochloromethane                         | 92                   | 2                      | 3                    | 95                   | 0                      | 103                  | 103                  | 1                      | 3                    |
| 2-Picoline                                   | 71                   | 5                      | 3                    | 66                   | 20                     | 62                   | 62                   | 8                      | 15                   |
| 1,2-Dibromoethane                            | 104                  | 1                      | 5                    | 108                  | 1                      | 108                  | 109                  | 0                      | 9                    |
| Chlorobenzene                                | 96                   | 1                      | 4                    | 97                   | 1                      | 109                  | 104                  | 1                      | 2                    |
| 1,1,1,2-Tetrachloroethane                    | 96                   | 1                      | 3                    | 97                   | 1                      | 98                   | 98                   | 1                      | 2                    |
| Ethylbenzene                                 | 102                  | 0                      | 2                    | 99                   | 1                      | 52                   | 96                   | 1                      | 1                    |
| <i>N</i> -Nitrosomethylethylamine            | 84                   | 6                      | 4                    | 92                   | 13                     | 46                   | 29                   | 1                      | 10                   |
| <i>m+p</i> -Xylenes                          | 101                  | 1                      | 2                    | 99                   | 1                      | 52                   | 94                   | 1                      | 1                    |
| Styrene                                      | 97                   | 1                      | 3                    | 96                   | 1                      | 49                   | 96                   | 0                      | 3                    |
| <i>o</i> -Xylene                             | 102                  | 1                      | 2                    | 100                  | 1                      | 53                   | 97                   | 1                      | 2                    |
| Isopropylbenzene                             | 101                  | 2                      | 1                    | 98                   | 1                      | 49                   | 87                   | 1                      | 4                    |
| Bromoform                                    | 94                   | 0                      | 5                    | 103                  | 2                      | 64                   | 101                  | 1                      | 8                    |
| <i>cis</i> -1,4-Dichloro-2-butene            | 106                  | 5                      | 6                    | 115                  | 1                      | 79                   | 116                  | 1                      | 9                    |
| <i>N</i> -Nitrosodiethylamine                | 104                  | 13                     | 4                    | 128                  | 16                     | 84                   | 45                   | 1                      | 11                   |
| 1,1,2,2-Tetrachloroethane                    | 93                   | 2                      | 5                    | 100                  | 1                      | 61                   | 101                  | 2                      | 8                    |
| 4-Bromo-1-fluorobenzene                      | 94                   | 2                      | 3                    | 93                   | 1                      | 45                   | 99                   | 0                      | 2                    |
| 1,2,3-Trichloropropane                       | 111                  | 6                      | 6                    | 120                  | 1                      | 86                   | 115                  | 1                      | 9                    |
| <i>n</i> -Propylbenzene                      | 100                  | 3                      | 1                    | 95                   | 0                      | 45                   | 85                   | 1                      | 5                    |
| <i>trans</i> -1,4-Dichloro-2-butene          | 103                  | 4                      | 5                    | 114                  | 3                      | 76                   | 119                  | 1                      | 10                   |
| 1,3,5-Trimethylbenzene                       | 103                  | 1                      | 1                    | 93                   | 2                      | 42                   | 91                   | 1                      | 2                    |
| Bromobenzene                                 | 97                   | 1                      | 3                    | 98                   | 0                      | 50                   | 102                  | 0                      | 2                    |
| 2-Chlorotoluene                              | 98                   | 1                      | 1                    | 90                   | 2                      | 41                   | 94                   | 1                      | 1                    |
| 4-Chlorotoluene                              | 98                   | 3                      | 2                    | 93                   | 1                      | 43                   | 95                   | 1                      | 2                    |
| Pentachloroethane                            | 88                   | 2                      | 2                    | 86                   | 3                      | 39                   | 72                   | 4                      | 2                    |
| <i>tert</i> -Butylbenzene                    | 103                  | 2                      | 2                    | 99                   | 1                      | 47                   | 83                   | 1                      | 4                    |
| 1,2,4-Trimethylbenzene                       | 104                  | 1                      | 2                    | 96                   | 2                      | 44                   | 91                   | 1                      | 2                    |

TABLE 6  
(continued)

| Compound                                   | Soil #1 <sup>a</sup> |                        |                      | Soil #2 <sup>b</sup> |                        |                      | Soil #3 <sup>c</sup> |                        |                      |
|--|----------------------|------------------------|----------------------|----------------------|------------------------|----------------------|----------------------|------------------------|----------------------|
|  | % Rec <sup>d</sup>   | Rel Error <sup>e</sup> | Sur Pre <sup>f</sup> | % Rec <sup>d</sup>   | Rel Error <sup>e</sup> | Sur Pre <sup>f</sup> | % Rec <sup>d</sup>   | Rel Error <sup>e</sup> | Sur Pre <sup>f</sup> |
| sec-Butylbenzene                           | 99                   | 4                      | 2                    | 93                   | 3                      | 43                   | 83                   | 1                      | 8                    |
| Aniline                                    | 106                  | 16                     | 10                   | 143                  | 29                     | 106                  | 15                   | 1                      | 10                   |
| <i>p</i> -Isopropyltoluene                 | 104                  | 2                      | 3                    | 101                  | 3                      | 48                   | 87                   | 2                      | 7                    |
| 1,3-Dichlorobenzene                        | 94                   | 3                      | 3                    | 88                   | 1                      | 38                   | 100                  | 1                      | 4                    |
| 1,4-Dichlorobenzene                        | 94                   | 2                      | 4                    | 90                   | 1                      | 41                   | 100                  | 1                      | 4                    |
| <i>n</i> -Butylbenzene                     | 97                   | 5                      | 3                    | 89                   | 4                      | 38                   | 83                   | 1                      | 8                    |
| 1,2-Dichlorobenzene                        | 95                   | 2                      | 4                    | 93                   | 0                      | 42                   | 103                  | 1                      | 5                    |
| Benzyl alcohol                             | 98                   | 6                      | 8                    | 128                  | 30                     | 82                   | 22                   | 1                      | 9                    |
| <i>N</i> -Nitrosodi- <i>n</i> -propylamine | 120                  | 16                     | 9                    | 185                  | 27                     | 168                  | 108                  | 3                      | 38                   |
| Acetophenone- <i>d</i> <sub>5</sub>        | 104                  | 10                     | 9                    | 167                  | 11                     | 136                  | 270                  | 7                      | 124                  |
| <i>o</i> -Toluidine                        | 118                  | 21                     | 12                   | 172                  | 45                     | 149                  | 19                   | 1                      | 14                   |
| 1,2-Dibromo-3-chloro propane               | 104                  | 7                      | 8                    | 143                  | 10                     | 106                  | 185                  | 3                      | 24                   |
| Hexachlorobutadiene                        | 88                   | 3                      | 14                   | 81                   | 12                     | 58                   | 75                   | 2                      | 8                    |
| 1,2,4-Trichlorobenzene                     | 88                   | 2                      | 13                   | 81                   | 1                      | 38                   | 104                  | 1                      | 8                    |
| Naphthalene- <i>d</i> <sub>8</sub>         | 88                   | 5                      | 17                   | 109                  | 5                      | 69                   | 141                  | 2                      | 12                   |
| Naphthalene                                | 88                   | 4                      | 18                   | 109                  | 2                      | 70                   | 132                  | 2                      | 12                   |
| 1,2,3-Trichlorobenzene                     | 83                   | 0                      | 18                   | 77                   | 2                      | 40                   | 111                  | 1                      | 10                   |
| <i>N</i> -Nitrosodibutylamine              | 133                  | 30                     | 44                   | 152                  | 51                     | 149                  | 11                   | 1                      | 11                   |
| 2-Methylnaphthalene                        | 60                   | 5                      | 20                   | 60                   | 0                      | 36                   | 62                   | 3                      | 29                   |

<sup>a</sup>Garden soil with 37% moisture and 21% organic matter. Three replicates were analyzed.

<sup>b</sup>Garden soil with 15% moisture and 16% organic matter. Three replicates were analyzed.

<sup>c</sup>Desert soil with 3% moisture and 1% organic matter. Seven replicates were analyzed.

<sup>d</sup>% Rec = Average of replicate accuracy results using surrogate corrections.

<sup>e</sup>Rel Error = Relative standard deviation of replicate analyses.

<sup>f</sup>Surr Prec = Average variation between the predicted analyte recoveries of the surrogate pairs for the replicate analyses. This precision value provides a measure of the inherent error in the overall measurement.

NA = Analyte not significantly present in vacuum distillate.

TABLE 7

RECOVERY OF ANALYTES SPIKED INTO OIL  
AND ANALYZED BY VACUUM DISTILLATION GC/MS

| Compound                                    | % Rec <sup>a</sup> | Relative Error <sup>b</sup> | Surrogate Precision <sup>c</sup> |
|---|--------------------|-----------------------------|----------------------------------|
| Dichlorodifluoromethane                     | 3                  | 0                           | 0                                |
| Chloromethane                               | 141                | 18                          | 2                                |
| Vinyl chloride                              | 137                | 11                          | 2                                |
| Bromomethane                                | 120                | 29                          | 0                                |
| Chloroethane                                | 128                | 44                          | 2                                |
| Trichlorofluoromethane                      | 313                | 176                         | 0                                |
| Diethyl ether                               | 103                | 5                           | 3                                |
| Acetone- <i>d</i> <sub>6</sub>              | 70                 | 8                           | 12                               |
| Acrolein                                    | 526                | 166                         | 28                               |
| Acetone                                     | 323                | 125                         | 42                               |
| 1,1-Dichloroethene                          | 116                | 4                           | 1                                |
| Iodomethane                                 | 105                | 6                           | 1                                |
| Allyl chloride                              | 119                | 16                          | 1                                |
| Acetonitrile                                | 24                 | 4                           | 4                                |
| Methylene chloride- <i>d</i> <sub>6</sub>   | 104                | 7                           | 2                                |
| Methylene chloride                          | 106                | 10                          | 2                                |
| Acrylonitrile                               | 88                 | 7                           | 14                               |
| <i>trans</i> -1,2-Dichloroethene            | 116                | 4                           | 0                                |
| 1,1-Dichloroethane                          | 103                | 2                           | 1                                |
| Methacrylonitrile                           | 94                 | 4                           | 4                                |
| 2-Butanone                                  | 92                 | 9                           | 13                               |
| Propionitrile                               | 85                 | 4                           | 13                               |
| Ethyl acetate- <sup>13</sup> C <sub>2</sub> | 84                 | 5                           | 3                                |
| 2,2-Dichloropropane                         | 97                 | 2                           | 1                                |
| <i>cis</i> -1,2-Dichloroethene              | 105                | 2                           | 1                                |
| Chloroform                                  | 97                 | 2                           | 2                                |

TABLE 7  
(continued)

| Compound                                     | % Rec <sup>a</sup> | Relative Error <sup>b</sup> | Surrogate Precision <sup>c</sup> |
|--|--------------------|-----------------------------|----------------------------------|
| Isobutyl alcohol                             | 115                | 11                          | 20                               |
| Bromochloromethane                           | 98                 | 3                           | 2                                |
| 1,1,1-Trichloroethane                        | 97                 | 3                           | 1                                |
| 1,1-Dichloropropene                          | 120                | 4                           | 3                                |
| Carbon tetrachloride                         | 93                 | 2                           | 1                                |
| Benzene- <i>d</i> <sub>6</sub>               | 100                | 2                           | 1                                |
| 1,2-Dichloroethane                           | 101                | 3                           | 3                                |
| Benzene                                      | 238                | 40                          | 0                                |
| Trichloroethene                              | 92                 | 3                           | 1                                |
| 1,2-Dichloropropane- <i>d</i> <sub>6</sub>   | 71                 | 13                          | 2                                |
| 1,2-Dichloropropane                          | 128                | 7                           | 3                                |
| Methyl methacrylate                          | 101                | 3                           | 4                                |
| Bromodichloromethane                         | 92                 | 1                           | 2                                |
| 1,4-Dioxane                                  | 88                 | 13                          | 14                               |
| Dibromomethane                               | 95                 | 4                           | 4                                |
| 4-Methyl-2-pentanone                         | 95                 | 5                           | 4                                |
| <i>trans</i> -1,3-Dichloropropene            | 103                | 2                           | 4                                |
| Toluene                                      | 164                | 16                          | 5                                |
| Pyridine                                     | 58                 | 42                          | 19                               |
| <i>cis</i> -1,3-Dichloropropene              | 94                 | 1                           | 4                                |
| Ethyl methacrylate                           | 109                | 2                           | 5                                |
| <i>N</i> -Nitrosodimethylamine               | 189                | 50                          | 7                                |
| 1,1,2-Trichloroethane- <i>d</i> <sub>3</sub> | 88                 | 2                           | 4                                |
| 2-Hexanone                                   | 106                | 6                           | 3                                |
| 1,1,2-Trichloroethane                        | 89                 | 2                           | 4                                |
| Tetrachloroethene                            | 68                 | 1                           | 1                                |
| 1,3-Dichloropropane                          | 99                 | 3                           | 4                                |
| Dibromochloromethane                         | 85                 | 1                           | 3                                |

TABLE 7  
(continued)

| Compound                            | % Rec <sup>a</sup> | Relative Error <sup>b</sup> | Surrogate Precision <sup>c</sup> |
|-------------------------------------|--------------------|-----------------------------|----------------------------------|
| 2-Picoline                          | 33                 | 24                          | 8                                |
| 1,2-Dibromoethane                   | 106                | 2                           | 3                                |
| Chlorobenzene                       | 101                | 1                           | 2                                |
| 1,1,1,2-Tetrachloroethane           | 83                 | 2                           | 1                                |
| Ethylbenzene                        | 114                | 3                           | 1                                |
| <i>N</i> -Nitrosomethylethylamine   | 192                | 48                          | 0                                |
| <i>m+p</i> -Xylenes                 | 122                | 3                           | 1                                |
| Styrene                             | 102                | 1                           | 2                                |
| <i>o</i> -Xylene                    | 115                | 3                           | 1                                |
| Isopropylbenzene                    | 109                | 5                           | 1                                |
| Bromoform                           | 88                 | 2                           | 3                                |
| <i>cis</i> -1,4-Dichloro-2-butene   | 103                | 3                           | 4                                |
| <i>N</i> -Nitrosodiethylamine       | 222                | 44                          | 30                               |
| 1,1,2,2-Tetrachloroethane           | 83                 | 5                           | 3                                |
| 4-Bromo-1-fluorobenzene             | 93                 | 2                           | 2                                |
| 1,2,3-Trichloropropane              | 103                | 4                           | 4                                |
| <i>n</i> -Propylbenzene             | 122                | 4                           | 1                                |
| <i>trans</i> -1,4-Dichloro-2-butene | 95                 | 3                           | 4                                |
| 1,3,5-Trimethylbenzene              | 93                 | 9                           | 2                                |
| Bromobenzene                        | 98                 | 2                           | 2                                |
| 2-Chlorotoluene                     | 78                 | 2                           | 1                                |
| 4-Chlorotoluene                     | 93                 | 2                           | 2                                |
| Pentachloroethane                   | 81                 | 4                           | 2                                |
| <i>tert</i> -Butylbenzene           | 120                | 55                          | 3                                |
| 1,2,4-Trimethylbenzene              | 127                | 8                           | 3                                |
| <i>sec</i> -Butylbenzene            | 89                 | 10                          | 3                                |
| Aniline                             | NA                 | NA                          | NA <sup>d</sup>                  |
| <i>p</i> -Isopropyltoluene          | NA                 | NA                          | NA                               |

TABLE 7  
(continued)

| Compound                                    | % Rec <sup>a</sup> | Relative Error <sup>b</sup> | Surrogate Precision <sup>c</sup> |
|---|--------------------|-----------------------------|----------------------------------|
| 1,3-Dichlorobenzene                         | 70                 | 2                           | 2                                |
| 1,4-Dichlorobenzene                         | 87                 | 3                           | 4                                |
| <i>n</i> -Butylbenzene                      | 105                | 4                           | 6                                |
| 1,2-Dichlorobenzene                         | 119                | 14                          | 7                                |
| Benzyl alcohol                              | NA                 | NA                          | NA                               |
| <i>n</i> -Nitroso-di- <i>n</i> -propylamine | 270                | 58                          | 51                               |
| Acetophenone- <i>d</i> <sub>5</sub>         | 175                | 31                          | 34                               |
| <i>o</i> -Toluidine                         | 108                | 69                          | 36                               |
| 1,2-Dibromo-3-chloropropane                 | 84                 | 14                          | 6                                |
| Hexachlorobutadiene                         | 119                | 6                           | 20                               |
| 1,2,4-Trichlorobenzene                      | 94                 | 5                           | 14                               |
| Naphthalene- <i>d</i> <sub>8</sub>          | 132                | 16                          | 29                               |
| Naphthalene                                 | 123                | 15                          | 32                               |
| 1,2,3-Trichlorobenzene                      | 80                 | 3                           | 21                               |
| <i>n</i> -Nitrosodibutylamine               | 2000               | 3600                        | 3200                             |
| 2-Methylnaphthalene                         | 667                | 1644                        | 4900                             |

<sup>a</sup>Average of seven replicate analyses of 1 g of cod liver oil.

<sup>b</sup>Relative standard deviation of replicate analyses.

<sup>c</sup>Average variation between the predicted analyte recoveries of the surrogate pairs for the replicate analyses. This precision value provides a measure of the inherent error in the overall measurement.

<sup>d</sup>NA = Compound could not be accurately measured due to spectral interferences.



TABLE 8  
METHOD DETECTION LIMITS<sup>a</sup>

| Compound                         | MDL (ppb)          |                   |                  |                        |
|----------------------------------|--------------------|-------------------|------------------|------------------------|
|                                  | Water <sup>b</sup> | Soil <sup>c</sup> | Oil <sup>d</sup> | Waste Oil <sup>e</sup> |
| Dichlorodifluoromethane          | 2.1                | 5.2               | 17               | 56                     |
| Chloromethane                    | 1.5                | 1.6               | 15               | 44                     |
| Vinyl chloride                   | 1.7                | 1.7               | 15               | 45                     |
| Bromomethane                     | 1.5                | 0.8               | 9.7              | 31                     |
| Chloroethane                     | 0.9                | 0.6               | 6.9              | 54                     |
| Trichlorofluoromethane           | 0.5                | 1.0               | 66               | 270                    |
| Diethyl ether                    | 0.4                | 2.4               | 2.4              | 9.2                    |
| Acrolein                         | 12                 | 75                | int <sup>f</sup> | int                    |
| Acetone                          | 3.0                | 2.7               | 23               | 97                     |
| 1,1-Dichloroethene               | 0.3                | 1.4               | 2.7              | 8.2                    |
| Iodomethane                      | 0.4                | 0.5               | 4.6              | 14                     |
| Allyl chloride                   | 1.0                | 2.0               | 20               | 66                     |
| Acetonitrile                     | 1.2                | 1.2               | int              | int                    |
| Methylene chloride               | 0.3                | 0.6               | 4.0              | 19                     |
| Acrylonitrile                    | 1.0                | 1.4               | 4.3              | 91                     |
| <i>trans</i> -1,2-Dichloroethene | 0.5                | 0.6               | 1.9              | 6.5                    |
| 1,1-Dichloroethane               | 0.6                | 0.2               | 1.5              | 5.5                    |
| Methacrylonitrile                | 0.6                | 0.5               | 6.2              | 47                     |
| 2-Butanone                       | 41                 | 5.9               | 35               | 190                    |
| Propionitrile                    | 0.7                | 0.9               | 7.1              | 140                    |
| 2,2-Dichloropropane              | 0.2                | 0.1               | 1.1              | 6.1                    |
| <i>cis</i> -1,2-Dichloroethene   | 0.1                | 0.1               | 1.5              | 5.6                    |
| Chloroform                       | 0.2                | 0.3               | 2.0              | 27                     |
| Isobutyl alcohol                 | 8.3                | 3.5               | int              | int                    |
| Bromochloromethane               | 0.2                | 0.1               | 1.0              | 3.6                    |
| 1,1,1-Trichloroethane            | 0.4                | 0.2               | 1.5              | 4.9                    |

TABLE 8  
(continued)

| Compound                          | MDL (ppb)          |                   |                  |                        |
|-----------------------------------|--------------------|-------------------|------------------|------------------------|
|                                   | Water <sup>b</sup> | Soil <sup>c</sup> | Oil <sup>d</sup> | Waste Oil <sup>e</sup> |
| 1,1-Dichloropropene               | 0.3                | 0.3               | 2.4              | 6.8                    |
| Carbon tetrachloride              | 0.2                | 0.2               | 1.1              | 6.0                    |
| 1,2-Dichloroethane                | 0.2                | 0.1               | 0.3              | 1.3                    |
| Benzene                           | 0.5                | 0.1               | 9.8              | 22                     |
| Trichloroethene                   | 0.2                | 0.1               | 1.1              | 6.3                    |
| 1,2-Dichloropropane               | 0.2                | 0.1               | 9.2              | 5.3                    |
| Methyl methacrylate               | 0.6                | 0.7               | 3.8              | 16                     |
| Bromodichloromethane              | 0.1                | 0.1               | 1.0              | 3.1                    |
| 1,4-Dioxane                       | 1.1                | 0.5               | 5.1              | 32                     |
| Dibromomethane                    | 0.2                | 0.1               | 0.7              | 6.3                    |
| 4-Methyl-2-pentanone              | 1.1                | 0.7               | 12               | 59                     |
| <i>trans</i> -1,3-Dichloropropene | 0.2                | 0.4               | 2.8              | 8.1                    |
| Toluene                           | 0.9                | 0.2               | 0.2              | 0.7                    |
| Pyridine                          | 2.8                | 2.6               | 36               | 130                    |
| <i>cis</i> -1,3-Dichloropropene   | 0.3                | 0.3               | 2.1              | 6.2                    |
| Ethyl methacrylate                | 0.4                | 1.1               | 7.8              | 10                     |
| <i>N</i> -Nitrosodimethylamine    | 33                 | 27                | 410              | 730                    |
| 2-Hexanone                        | 1.4                | 1.4               | 14               | 66                     |
| 1,1,2-Trichloroethane             | 0.2                | 0.1               | 1.7              | 3.9                    |
| Tetrachloroethene                 | 0.6                | 0.7               | 1.7              | 4.4                    |
| 1,3-Dichloropropane               | 0.2                | 0.1               | 1.2              | 5.1                    |
| Dibromochloromethane              | 0.2                | 0.2               | 2.1              | 7.1                    |
| 2-Picoline                        | NA <sup>g</sup>    | 100               | NA               | NA                     |
| 1,2-Dibromoethane                 | 0.2                | 0.1               | 0.9              | 3.1                    |
| Chlorobenzene                     | 0.3                | 0.2               | 2.0              | 16                     |
| 1,1,1,2-Tetrachloroethane         | 0.2                | 0.1               | 2.0              | 6.6                    |
| Ethylbenzene                      | 0.3                | 0.2               | 3.2              | 2.4                    |
| <i>N</i> -Nitrosomethylethylamine | 28                 | 16                | 450              | 57                     |

TABLE 8  
(continued)

| Compound                                  | MDL (ppb)          |                   |                  |                        |
|---|--------------------|-------------------|------------------|------------------------|
|   | Water <sup>b</sup> | Soil <sup>c</sup> | Oil <sup>d</sup> | Waste Oil <sup>e</sup> |
| <i>m+p</i> -Xylenes                       | 0.6                | 0.2               | 5.8              | 6.4                    |
| Styrene                                   | 0.1                | 0.1               | 1.2              | 3.5                    |
| <i>o</i> -Xylene                          | 0.5                | 0.2               | 5.0              | 7.3                    |
| Isopropylbenzene                          | 0.3                | 0.2               | 1.4              | 4.7                    |
| Bromoform                                 | 0.5                | 0.2               | 2.0              | 9.3                    |
| <i>cis</i> -1,4-Dichloro-2-butene         | 0.7                | 0.5               | 2.5              | 17                     |
| <i>N</i> -Nitrosodiethylamine             | 22                 | 11                | 420              | 860                    |
| 1,1,2,2-Tetrachloroethane                 | 0.4                | 0.2               | 2.9              | 19                     |
| 4-Bromo-1-fluorobenzene                   | 0.0                | 0.0               | 0.4              | 2.1                    |
| 1,2,3-Trichloropropane                    | 1.0                | 0.9               | 14               | 25                     |
| <i>n</i> -Propylbenzene                   | 0.3                | 0.2               | 4.6              | 10                     |
| <i>trans</i> -1,4-Dichloro-2-butene       | 0.8                | 0.6               | 9.0              | 17                     |
| 1,3,5-Trimethylbenzene                    | 0.4                | 0.3               | 22               | 38                     |
| Bromobenzene                              | 0.2                | 0.1               | 0.7              | 3.5                    |
| 2-Chlorotoluene                           | 0.2                | 0.2               | 1.7              | 7.9                    |
| 4-Chlorotoluene                           | 0.2                | 0.2               | 1.0              | 8.4                    |
| Pentachloroethane                         | 1.1                | 1.2               | 6.6              | 24                     |
| <i>tert</i> -Butylbenzene                 | 0.2                | 0.3               | 26               | 58                     |
| 1,2,4-Trimethylbenzene                    | 0.5                | 0.2               | 30               | 180                    |
| <i>sec</i> -Butylbenzene                  | 0.2                | 0.3               | 4.0              | 55                     |
| Aniline                                   | 23                 | 13.2              | int              | int                    |
| <i>p</i> -Isopropyltoluene                | 0.2                | 0.3               | 16               | 62                     |
| 1,3-Dichlorobenzene                       | 0.1                | 0.1               | 1.3              | 5.9                    |
| 1,4-Dichlorobenzene                       | 0.2                | 0.1               | 1.0              | 6.8                    |
| <i>n</i> -Butylbenzene                    | 0.4                | 0.4               | 4.5              | 13                     |
| 1,2-Dichlorobenzene                       | 0.3                | 0.2               | 10               | 33                     |
| Benzyl alcohol                            | 20                 | 11.8              | int              | int                    |
| <i>N</i> -Nitro-di- <i>n</i> -propylamine | 26                 | 14                | 290              | 1300                   |

TABLE 8  
(continued)

| Compound                      | MDL (ppb)          |                   |                  |                        |
|-------------------------------|--------------------|-------------------|------------------|------------------------|
|                               | Water <sup>b</sup> | Soil <sup>c</sup> | Oil <sup>d</sup> | Waste Oil <sup>e</sup> |
| <i>o</i> -Toluidine           | 26                 | 12                | 530              | 2100                   |
| 1,2-Dibromo-3-chloropropane   | 0.7                | 0.3               | 2.7              | 15                     |
| Hexachlorobutadiene           | 0.4                | 0.4               | 3.1              | 14                     |
| 1,2,4-Trichlorobenzene        | 0.3                | 0.3               | 3.2              | 7.4                    |
| Naphthalene                   | 0.6                | 0.3               | 5.4              | 9.3                    |
| 1,2,3-Trichlorobenzene        | 0.4                | 0.3               | 5.6              | 19.5                   |
| <i>N</i> -Nitrosodibutylamine | 36                 | 14                | NA               | NA                     |
| 2-Methylnaphthalene           | 1.8                | 1.0               | NA               | NA                     |

<sup>a</sup> Method detection limits reported here are equal to 3 times the average standard deviation of 3 sets of 7 replicate analyses performed on three nonconsecutive days and are for illustrative purposes only. (Note: This is similar to, but not the same as, the procedures described in either Chapter One or 40 CFR 136). Units for water are µg/L, and µg/kg for all other matrices.

<sup>b</sup> Results are for 5-mL water samples.

<sup>c</sup> Results are for 5-g soil samples.

<sup>d</sup> Results are for 1-g samples.

<sup>e</sup> Results are for 0.2-g samples of cod liver oil.

<sup>f</sup> Int = Spectral interferences prevented accurate integrations.

<sup>g</sup> NA = Compound not significantly present in vacuum distillate.

TABLE 9

## RECOVERY OF ANALYTES SPIKED INTO WATER SOLUTIONS AND ANALYZED BY VACUUM DISTILLATION GC/MS

| Compound                                  | Water <sup>a</sup> |                        |                        | Water/Glycerin <sup>b</sup> |                        |                        | Water/Salt <sup>c</sup> |                        |                        | Water/Soap <sup>d</sup> |                        |                        |
|---|--------------------|------------------------|------------------------|-----------------------------|------------------------|------------------------|-------------------------|------------------------|------------------------|-------------------------|------------------------|------------------------|
|   | % Rec <sup>e</sup> | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>          | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>      | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>      | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> |
| Dichlorodifluoromethane                   | 76                 | 9                      | 1                      | 84                          | 8                      | 1                      | 85                      | 6                      | 1                      | 56                      | 7                      | 1                      |
| Chloromethane                             | 81                 | 6                      | 1                      | 86                          | 8                      | 1                      | 83                      | 10                     | 1                      | 77                      | 3                      | 1                      |
| Vinyl chloride                            | 78                 | 5                      | 1                      | 81                          | 3                      | 1                      | 74                      | 4                      | 1                      | 81                      | 4                      | 1                      |
| Bromomethane                              | 101                | 5                      | 1                      | 103                         | 2                      | 0                      | 116                     | 47                     | 1                      | 102                     | 4                      | 1                      |
| Chloroethane                              | 95                 | 5                      | 1                      | 96                          | 2                      | 1                      | 112                     | 52                     | 1                      | 95                      | 5                      | 1                      |
| Trichlorofluoromethane                    | 122                | 52                     | 1                      | 98                          | 1                      | 1                      | 120                     | 58                     | 1                      | 96                      | 3                      | 1                      |
| Diethyl ether                             | 106                | 17                     | 2                      | 98                          | 12                     | 1                      | 14                      | 8                      | 0                      | 17                      | 14                     | 1                      |
| Acrolein                                  | 111                | 16                     | 3                      | 114                         | 5                      | 1                      | 20                      | 10                     | 2                      | 49                      | 6                      | 2                      |
| Acetone                                   | 114                | 17                     | 5                      | 286                         | 41                     | 16                     | 88                      | 5                      | 20                     | 71                      | 10                     | 3                      |
| 1,1-Dichloroethene                        | 102                | 10                     | 1                      | 98                          | 6                      | 1                      | 20                      | 12                     | 0                      | 93                      | 9                      | 1                      |
| Iodomethane                               | 103                | 7                      | 1                      | 104                         | 7                      | 0                      | 98                      | 4                      | 1                      | 103                     | 2                      | 0                      |
| Allyl chloride                            | 102                | 10                     | 1                      | 101                         | 6                      | 1                      | 95                      | 4                      | 1                      | 101                     | 3                      | 1                      |
| Acetonitrile                              | 122                | 21                     | 6                      | 189                         | 2                      | 7                      | 82                      | 11                     | 17                     | 99                      | 8                      | 4                      |
| Methylene chloride- <i>d</i> <sub>2</sub> | 103                | 7                      | 1                      | 104                         | 9                      | 0                      | 99                      | 7                      | 1                      | 102                     | 6                      | 2                      |
| Methylene chloride                        | 99                 | 9                      | 1                      | 101                         | 10                     | 0                      | 95                      | 10                     | 1                      | 98                      | 8                      | 2                      |
| Acrylonitrile                             | 97                 | 1                      | 7                      | 95                          | 3                      | 7                      | 112                     | 21                     | 27                     | 93                      | 3                      | 4                      |
| <i>trans</i> -1,2-Dichloroethane          | 100                | 4                      | 1                      | 100                         | 5                      | 0                      | 94                      | 8                      | 1                      | 93                      | 6                      | 1                      |
| 1,1-Dichloroethane                        | 102                | 5                      | 1                      | 102                         | 5                      | 0                      | 101                     | 4                      | 0                      | 101                     | 1                      | 1                      |
| Methacrylonitrile                         | 101                | 3                      | 2                      | 101                         | 1                      | 1                      | 108                     | 7                      | 7                      | 104                     | 2                      | 4                      |
| 2-Butanone                                | 68                 | 43                     | 7                      | 106                         | 31                     | 10                     | 105                     | 27                     | 25                     | 97                      | 2                      | 4                      |

TABLE 9  
(continued)

| Compound                                   | Water <sup>a</sup> |                        |                        | Water/Glycerin <sup>b</sup> |                        |                        | Water/Salt <sup>c</sup> |                        |                        | Water/Soap <sup>d</sup> |                        |                        |
|--|--------------------|------------------------|------------------------|-----------------------------|------------------------|------------------------|-------------------------|------------------------|------------------------|-------------------------|------------------------|------------------------|
|  | % Rec <sup>e</sup> | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>          | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>      | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>      | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> |
| Propionitrile                              | 100                | 6                      | 6                      | 109                         | 9                      | 14                     | 111                     | 31                     | 22                     | 103                     | 3                      | 4                      |
| 2,2-Dichloropropane                        | 100                | 1                      | 1                      | 99                          | 1                      | 1                      | 100                     | 1                      | 1                      | 102                     | 1                      | 1                      |
| <i>cis</i> -1,2-Dichloroethene             | 100                | 1                      | 1                      | 100                         | 1                      | 0                      | 97                      | 2                      | 0                      | 103                     | 0                      | 1                      |
| Chloroform                                 | 100                | 1                      | 1                      | 100                         | 2                      | 1                      | 100                     | 2                      | 0                      | 103                     | 1                      | 2                      |
| Isobutyl alcohol                           | 86                 | 7                      | 5                      | 137                         | 17                     | 5                      | 116                     | 21                     | 30                     | 76                      | 10                     | 3                      |
| Bromochloromethane                         | 102                | 1                      | 1                      | 102                         | 1                      | 0                      | 100                     | 0                      | 1                      | 102                     | 1                      | 1                      |
| 1,1,1-Trichloroethane                      | 100                | 1                      | 1                      | 99                          | 1                      | 1                      | 98                      | 3                      | 1                      | 99                      | 1                      | 1                      |
| 1,1-Dichloropropene                        | 95                 | 3                      | 1                      | 96                          | 3                      | 1                      | 94                      | 3                      | 1                      | 99                      | 3                      | 1                      |
| Carbon tetrachloride                       | 100                | 0                      | 1                      | 100                         | 2                      | 1                      | 100                     | 2                      | 1                      | 88                      | 2                      | 1                      |
| Benzene- <i>d</i> <sub>6</sub>             | 99                 | 1                      | 1                      | 99                          | 1                      | 1                      | 99                      | 1                      | 0                      | 100                     | 1                      | 1                      |
| 1,2-Dichloroethane                         | 101                | 1                      | 1                      | 101                         | 1                      | 1                      | 99                      | 1                      | 1                      | 100                     | 1                      | 2                      |
| Benzene                                    | 99                 | 0                      | 1                      | 100                         | 1                      | 1                      | 99                      | 2                      | 0                      | 99                      | 1                      | 1                      |
| Trichloroethene                            | 100                | 1                      | 1                      | 99                          | 1                      | 0                      | 98                      | 1                      | 1                      | 109                     | 1                      | 0                      |
| 1,2-Dichloropropane- <i>d</i> <sub>6</sub> | 99                 | 2                      | 1                      | 99                          | 2                      | 0                      | 99                      | 2                      | 1                      | 101                     | 2                      | 2                      |
| 1,2-Dichloropropane                        | 100                | 1                      | 1                      | 100                         | 1                      | 0                      | 99                      | 1                      | 1                      | 101                     | 1                      | 2                      |
| Methyl methacrylate                        | 106                | 7                      | 2                      | 128                         | 10                     | 1                      | 114                     | 4                      | 5                      | 106                     | 2                      | 5                      |
| Bromodichloromethane                       | 102                | 1                      | 1                      | 100                         | 1                      | 0                      | 102                     | 2                      | 1                      | 101                     | 1                      | 2                      |
| 1,4-Dioxane                                | 101                | 8                      | 8                      | 156                         | 15                     | 83                     | 96                      | 18                     | 16                     | 102                     | 3                      | 14                     |
| Dibromomethane                             | 102                | 1                      | 2                      | 101                         | 1                      | 1                      | 99                      | 1                      | 3                      | 100                     | 1                      | 5                      |
| 4-Methyl-2-pentanone                       | 102                | 5                      | 3                      | 102                         | 3                      | 1                      | 116                     | 1                      | 9                      | 110                     | 2                      | 5                      |
| <i>trans</i> -1,3-Dichloropropene          | 99                 | 1                      | 1                      | 100                         | 0                      | 1                      | 99                      | 2                      | 1                      | 103                     | 1                      | 1                      |

TABLE 9  
(continued)

| Compound                                     | Water <sup>a</sup> |                        |                        | Water/Glycerin <sup>b</sup> |                        |                        | Water/Salt <sup>c</sup> |                        |                        | Water/Soap <sup>d</sup> |                        |                        |
|--|--------------------|------------------------|------------------------|-----------------------------|------------------------|------------------------|-------------------------|------------------------|------------------------|-------------------------|------------------------|------------------------|
|  | % Rec <sup>e</sup> | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>          | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>      | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>      | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> |
| Toluene                                      | 98                 | 2                      | 1                      | 99                          | 1                      | 1                      | 97                      | 3                      | 1                      | 97                      | 1                      | 1                      |
| Pyridine                                     | 61                 | 20                     | 16                     | NA                          | NA                     | NA                     | 104                     | 24                     | 37                     | 128                     | 7                      | 36                     |
| <i>cis</i> -1,3-Dichloropropene              | 99                 | 1                      | 1                      | 99                          | 1                      | 1                      | 97                      | 2                      | 1                      | 100                     | 1                      | 2                      |
| Ethyl methacrylate                           | 109                | 9                      | 2                      | 156                         | 17                     | 1                      | 109                     | 25                     | 3                      | 105                     | 2                      | 4                      |
| <i>N</i> -Nitrosodimethylamine               | 75                 | 8                      | 2                      | 97                          | 8                      | 1                      | 105                     | 32                     | 10                     | 69                      | 9                      | 4                      |
| 1,1,2-Trichloroethane- <i>d</i> <sub>3</sub> | 100                | 1                      | 2                      | 100                         | 2                      | 1                      | 101                     | 2                      | 3                      | 99                      | 1                      | 5                      |
| 2-Hexanone                                   | 102                | 9                      | 3                      | 99                          | 4                      | 1                      | 118                     | 4                      | 11                     | 112                     | 3                      | 5                      |
| 1,1,2-Trichloroethane                        | 100                | 2                      | 2                      | 100                         | 1                      | 1                      | 101                     | 1                      | 2                      | 101                     | 1                      | 5                      |
| Tetrachloroethene                            | 98                 | 11                     | 1                      | 98                          | 14                     | 1                      | 106                     | 34                     | 1                      | 200                     | 36                     | 0                      |
| 1,3-Dichloropropane                          | 98                 | 1                      | 2                      | 99                          | 1                      | 1                      | 98                      | 2                      | 3                      | 98                      | 1                      | 5                      |
| Dibromochloromethane                         | 102                | 1                      | 1                      | 101                         | 2                      | 1                      | 104                     | 1                      | 1                      | 102                     | 1                      | 2                      |
| 2-Picoline                                   | NA                 | NA                     | NA                     | NA                          | NA                     | NA                     | 169                     | 69                     | 26                     | 217                     | 28                     | 33                     |
| 1,2-Dibromoethane                            | 100                | 1                      | 2                      | 100                         | 1                      | 1                      | 101                     | 1                      | 2                      | 104                     | 1                      | 5                      |
| Chlorobenzene                                | 100                | 1                      | 1                      | 100                         | 1                      | 1                      | 99                      | 1                      | 1                      | 102                     | 0                      | 2                      |
| 1,1,1,2-Tetrachloroethane                    | 101                | 1                      | 1                      | 100                         | 1                      | 0                      | 102                     | 1                      | 1                      | 100                     | 1                      | 2                      |
| Ethylbenzene                                 | 97                 | 2                      | 1                      | 99                          | 2                      | 1                      | 98                      | 1                      | 0                      | 97                      | 2                      | 1                      |
| <i>N</i> -Nitrosomethylethylamine            | 70                 | 9                      | 4                      | 111                         | 10                     | 20                     | 130                     | 35                     | 25                     | 79                      | 1                      | 4                      |
| <i>m+p</i> -Xylenes                          | 98                 | 2                      | 1                      | 99                          | 1                      | 1                      | 97                      | 1                      | 0                      | 101                     | 1                      | 1                      |
| Styrene                                      | 98                 | 0                      | 1                      | 99                          | 1                      | 1                      | 97                      | 3                      | 1                      | 102                     | 0                      | 3                      |
| <i>o</i> -Xylene                             | 98                 | 1                      | 1                      | 99                          | 1                      | 1                      | 98                      | 1                      | 1                      | 106                     | 1                      | 2                      |
| Isopropylbenzene                             | 97                 | 2                      | 1                      | 99                          | 2                      | 1                      | 95                      | 3                      | 1                      | 84                      | 2                      | 2                      |

TABLE 9  
(continued)

| Compound                            | Water <sup>a</sup> |                        |                        | Water/Glycerin <sup>b</sup> |                        |                        | Water/Salt <sup>c</sup> |                        |                        | Water/Soap <sup>d</sup> |                        |                        |
|-------------------------------------|--------------------|------------------------|------------------------|-----------------------------|------------------------|------------------------|-------------------------|------------------------|------------------------|-------------------------|------------------------|------------------------|
|                                     | % Rec <sup>e</sup> | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>          | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>      | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>      | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> |
| Bromoform                           | 103                | 2                      | 2                      | 101                         | 2                      | 1                      | 109                     | 1                      | 2                      | 108                     | 2                      | 6                      |
| <i>cis</i> -1,4-Dichloro-2-butene   | 102                | 4                      | 2                      | 102                         | 2                      | 1                      | 110                     | 2                      | 1                      | 114                     | 4                      | 6                      |
| <i>N</i> -Nitrosodiethylamine       | 78                 | 9                      | 6                      | 133                         | 11                     | 60                     | 128                     | 31                     | 18                     | 78                      | 2                      | 9                      |
| 1,1,2,2-Tetrachloroethane           | 101                | 2                      | 2                      | 100                         | 3                      | 1                      | 111                     | 2                      | 2                      | 82                      | 3                      | 4                      |
| 4-Bromo-1-fluorobenzene             | 101                | 1                      | 1                      | 101                         | 1                      | 1                      | 101                     | 1                      | 1                      | 102                     | 1                      | 3                      |
| 1,2,3-Trichloropropane              | 97                 | 6                      | 2                      | 99                          | 3                      | 1                      | 105                     | 6                      | 2                      | 112                     | 3                      | 6                      |
| <i>n</i> -Propylbenzene             | 97                 | 2                      | 1                      | 98                          | 2                      | 1                      | 94                      | 3                      | 1                      | 81                      | 3                      | 2                      |
| <i>trans</i> -1,4-Dichloro-2-butene | 101                | 4                      | 2                      | 102                         | 2                      | 1                      | 111                     | 2                      | 2                      | 115                     | 4                      | 7                      |
| 1,3,5-Trimethylbenzene              | 98                 | 3                      | 1                      | 99                          | 2                      | 1                      | 96                      | 3                      | 1                      | 83                      | 1                      | 1                      |
| Bromobenzene                        | 101                | 0                      | 1                      | 101                         | 0                      | 1                      | 100                     | 1                      | 1                      | 104                     | 1                      | 3                      |
| 2-Chlorotoluene                     | 96                 | 4                      | 1                      | 99                          | 3                      | 1                      | 95                      | 3                      | 1                      | 88                      | 2                      | 2                      |
| 4-Chlorotoluene                     | 101                | 2                      | 1                      | 100                         | 2                      | 1                      | 98                      | 1                      | 1                      | 94                      | 2                      | 2                      |
| Pentachloroethane                   | 103                | 10                     | 1                      | 100                         | 9                      | 1                      | 94                      | 18                     | 1                      | 29                      | 8                      | 1                      |
| <i>tert</i> -Butylbenzene           | 99                 | 3                      | 1                      | 100                         | 3                      | 1                      | 95                      | 5                      | 1                      | 66                      | 2                      | 1                      |
| 1,2,4-Trimethylbenzene              | 98                 | 2                      | 1                      | 99                          | 2                      | 1                      | 96                      | 2                      | 1                      | 88                      | 2                      | 2                      |
| <i>sec</i> -Butylbenzene            | 98                 | 3                      | 1                      | 99                          | 2                      | 1                      | 93                      | 3                      | 2                      | 74                      | 2                      | 2                      |
| Aniline                             | 119                | 40                     | 18                     | 74                          | 15                     | 65                     | 79                      | 37                     | 30                     | 97                      | 9                      | 29                     |
| <i>p</i> -Isopropyltoluene          | 97                 | 0                      | 2                      | 98                          | 4                      | 2                      | 93                      | 3                      | 2                      | 81                      | 2                      | 4                      |
| 1,3-Dichlorobenzene                 | 101                | 1                      | 1                      | 100                         | 1                      | 1                      | 99                      | 1                      | 1                      | 98                      | 1                      | 3                      |
| 1,4-Dichlorobenzene                 | 101                | 1                      | 1                      | 101                         | 1                      | 1                      | 100                     | 2                      | 1                      | 105                     | 1                      | 3                      |
| <i>n</i> -Butylbenzene              | 97                 | 2                      | 2                      | 98                          | 3                      | 2                      | 91                      | 2                      | 2                      | 74                      | 2                      | 3                      |



TABLE 9  
(continued)

| Compound                                    | Water <sup>a</sup> |                        |                        | Water/Glycerin <sup>b</sup> |                        |                        | Water/Salt <sup>c</sup> |                        |                        | Water/Soap <sup>d</sup> |                        |                        |
|---|--------------------|------------------------|------------------------|-----------------------------|------------------------|------------------------|-------------------------|------------------------|------------------------|-------------------------|------------------------|------------------------|
|   | % Rec <sup>e</sup> | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>          | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>      | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> | % Rec <sup>e</sup>      | Rel Error <sup>f</sup> | Surr Prec <sup>g</sup> |
| 1,2-Dichlorobenzene                         | 100                | 1                      | 1                      | 100                         | 1                      | 1                      | 100                     | 1                      | 2                      | 102                     | 1                      | 5                      |
| Benzyl alcohol                              | 128                | 28                     | 19                     | 167                         | 14                     | 125                    | 65                      | 35                     | 15                     | 93                      | 5                      | 23                     |
| <i>N</i> -Nitroso-di- <i>n</i> -propylamine | 68                 | 14                     | 5                      | 108                         | 9                      | 25                     | 56                      | 15                     | 29                     | 112                     | 5                      | 15                     |
| Acetophenone- <i>d</i> <sub>5</sub>         | 71                 | 20                     | 7                      | 81                          | 7                      | 7                      | 99                      | 66                     | 23                     | 156                     | 7                      | 17                     |
| <i>o</i> -Toluidine                         | 127                | 42                     | 21                     | 66                          | 20                     | 61                     | 97                      | 49                     | 41                     | 115                     | 15                     | 37                     |
| 1,2-Dibromo-3-chloropropane                 | 101                | 9                      | 3                      | 99                          | 5                      | 3                      | 111                     | 25                     | 4                      | 156                     | 7                      | 15                     |
| Hexachlorobutadiene                         | 101                | 2                      | 2                      | 102                         | 4                      | 3                      | 92                      | 3                      | 3                      | 74                      | 2                      | 4                      |
| 1,2,4-Trichlorobenzene                      | 101                | 1                      | 2                      | 100                         | 1                      | 3                      | 102                     | 1                      | 3                      | 104                     | 1                      | 5                      |
| Naphthalene- <i>d</i> <sub>8</sub>          | 102                | 5                      | 2                      | 100                         | 2                      | 4                      | 112                     | 5                      | 5                      | 127                     | 3                      | 10                     |
| Naphthalene                                 | 101                | 4                      | 2                      | 101                         | 2                      | 4                      | 110                     | 2                      | 5                      | 125                     | 3                      | 9                      |
| 1,2,3-Trichlorobenzene                      | 100                | 2                      | 2                      | 100                         | 1                      | 4                      | 100                     | 3                      | 5                      | 93                      | 3                      | 8                      |
| <i>N</i> -Nitrosodibutylamine               | 208                | 109                    | 43                     | 400                         | 32                     | 384                    | 90                      | 69                     | 67                     | 98                      | 21                     | 43                     |
| 2-Methylnaphthalene                         | 84                 | 6                      | 8                      | 91                          | 10                     | 12                     | 98                      | 27                     | 24                     | 55                      | 3                      | 11                     |

<sup>a</sup>5-mL water samples

<sup>b</sup>1 g of glycerin added to 5 mL of water

<sup>c</sup>1 g of salt added to 5 mL of water

<sup>d</sup>0.2 g of concentrated soap added to 5 mL of water

<sup>e</sup>Average of four replicate analyses

<sup>f</sup>Relative standard deviation of replicate analyses

<sup>g</sup>Average variation between the predicted analyte recoveries of the surrogate pairs for the replicate analyses. This precision value provides a measure of the inherent error in the overall measurement.

<sup>h</sup>NA = compound not significantly present in vacuum distillate.

TABLE 10  
METHOD PERFORMANCE IN FISH TISSUE

| Compound                                  | Surrogate Type | Spike (ppb) <sup>c</sup> | Using water standards <sup>a</sup>  |                  | Using tuna standards <sup>b</sup>    |                                     |                  | MDL vs. Water Std <sup>g</sup> | MDL vs. Tuna Std |                                      |
|---|----------------|--------------------------|-------------------------------------|------------------|--------------------------------------|-------------------------------------|------------------|--------------------------------|------------------|--------------------------------------|
|   |                |                          | Mean Compound Recovery <sup>d</sup> | RSD <sup>e</sup> | Mean Surrogate Recovery <sup>f</sup> | Mean Compound Recovery <sup>d</sup> | RSD <sup>e</sup> |                                |                  | Mean Surrogate Recovery <sup>f</sup> |
| Dichlorodifluoromethane                   |                | 1000                     | 109                                 | 22               | 24                                   | 116                                 | 17               | 16                             | 5                | 6                                    |
| Chloromethane                             |                | 1000                     | 105                                 | 16               | 16                                   | 102                                 | 13               | 10                             | 5                | 5                                    |
| Vinyl chloride                            |                | 1000                     | 105                                 | 20               | 21                                   | 115                                 | 15               | 14                             | 4                | 5                                    |
| Bromomethane                              |                | 1000                     | 90                                  | 19               | 11                                   | 89                                  | 18               | 7                              | 7                | 8                                    |
| Chloroethane                              |                | 1000                     | 102                                 | 21               | 18                                   | 110                                 | 17               | 12                             | 5                | 5                                    |
| Trichlorofluoromethane                    |                | 1000                     | 97                                  | 24               | 21                                   | 125                                 | 18               | 16                             | 5                | 5                                    |
| Diethyl ether- <i>d</i> <sub>10</sub>     | Check          | 250                      | 113                                 | 9                | 4                                    | 108                                 | 9                | 3                              | ND               | ND                                   |
| Ether                                     |                | 500                      | 104                                 | 10               | 4                                    | 106                                 | 10               | 3                              | 17               | 18                                   |
| Acetone- <i>d</i> <sub>6</sub>            | Check          | 2500                     | 41                                  | 27               | 0                                    | 149                                 | 20               | 1                              | ND               | ND                                   |
| Acetone                                   |                | Cont                     | --                                  | --               | --                                   | --                                  | --               | --                             | 67               | 60                                   |
| 1,1-Dichloroethene                        |                | 500                      | 44                                  | 54               | 8                                    | 134                                 | 31               | 15                             | 8                | 7                                    |
| Iodomethane                               |                | 500                      | 10                                  | 101              | 1                                    | 57                                  | 129              | 3                              | 9                | 13                                   |
| Allyl chloride                            |                | 500                      | 55                                  | 75               | 9                                    | 96                                  | 79               | 9                              | 14               | 3                                    |
| Acetonitrile                              |                | Int                      | --                                  | --               | --                                   | --                                  | --               | --                             | ND               | ND                                   |
| Methylene chloride- <i>d</i> <sub>6</sub> | Check          | 250                      | 94                                  | 18               | 3                                    | 109                                 | 19               | 2                              | ND               | ND                                   |
| Methylene chloride                        |                | 500                      | 74                                  | 24               | 2                                    | 91                                  | 22               | 2                              | 2                | 1                                    |
| Acrylonitrile                             |                | 500                      | 65                                  | 25               | 0                                    | 75                                  | 28               | 0                              | 21               | 15                                   |
| <i>trans</i> -1,2-Dichloroethene          |                | 500                      | 77                                  | 29               | 7                                    | 84                                  | 32               | 5                              | 2                | 2                                    |
| Nitromethane- <i>d</i> <sub>3</sub>       | Check          | 250                      | 121                                 | 42               | 3                                    | 133                                 | 41               | 2                              | ND               | ND                                   |
| 1,1-Dichloroethane                        |                | 500                      | 89                                  | 74               | 1                                    | 53                                  | 40               | 0                              | 6                | 4                                    |
| Hexafluorobenzene                         | Alpha          | 250                      | --                                  | --               | --                                   | --                                  | --               | --                             | ND               | ND                                   |
| Tetrahydrofuran- <i>d</i> <sub>8</sub>    | Alpha          | 250                      | --                                  | --               | --                                   | --                                  | --               | --                             | ND               | ND                                   |
| Methacrylonitrile                         |                | 500                      | 103                                 | 17               | 5                                    | 100                                 | 17               | 5                              | 8                | 8                                    |
| 2-Butanone                                |                | 500                      | 122                                 | 11               | 2                                    | 149                                 | 10               | 1                              | 9                | 6                                    |

TABLE 10  
(continued)

| Compound                                   | Surrogate Type | Spike<br>(ppb) <sup>c</sup> | Using water standards <sup>a</sup>        |                  | Using tuna standards <sup>b</sup>          |   |                  |  | MDL vs.<br>Water<br>Std <sup>g</sup> | MDL vs.<br>Tuna<br>Std |
|--|----------------|-----------------------------|---|------------------|--|---|------------------|--|--------------------------------------|------------------------|
|  |                |                             | Mean<br>Compound<br>Recovery <sup>d</sup> | RSD <sup>e</sup> | Mean<br>Surrogate<br>Recovery <sup>f</sup> | Mean<br>Compound<br>Recovery <sup>d</sup> | RSD <sup>e</sup> | Mean<br>Surrogate<br>Recovery <sup>f</sup> |                                      |                        |
| Propionitrile                              |                | 500                         | 113                                       | 8                | 5  | 120                                       | 8                | 3  | 3                                    | 3                      |
| Ethyl acetate- <sup>13</sup> C             | Check          | 2500                        | 76  | 18               | 1  | 95  | 18               | 0  | ND                                   | ND                     |
| 2,2-Dichloropropane                        |                | 500                         | 94  | 16               | 14   | 108                                       | 13               | 10   | 3                                    | 2                      |
| <i>cis</i> -1,2-Dichloroethene             |                | 500                         | 102                                       | 6                | 3  | 100                                       | 7                | 2  | 2                                    | 2                      |
| Chloroform                                 |                | 500                         | 101                                       | 6                | 4  | 100                                       | 7                | 3  | 2                                    | 2                      |
| Pentafluorobenzene                         | Alpha          | 250                         | --  | --               | --   | --  | --               | --   | ND                                   | ND                     |
| Bromochloromethane                         |                | 500                         | 100                                       | 5                | 2  | 99  | 5                | 2  | 1                                    | 1                      |
| 1,1,1-Trichloroethane                      |                | 500                         | 91  | 18               | 14   | 113                                       | 13               | 10   | 2                                    | 2                      |
| 1,1-Dichloropropene                        |                | 500                         | 99  | 21               | 18   | 128                                       | 15               | 15   | 3                                    | 3                      |
| Carbon tetrachloride                       |                | 500                         | 80  | 22               | 15   | 122                                       | 17               | 14   | 3                                    | 5                      |
| Benzene- <i>d</i> <sub>6</sub>             | Alpha          | 500                         | --  | --               | --   | --  | --               | --   | ND                                   | ND                     |
| 1,2-Dichloroethane- <i>d</i> <sub>4</sub>  | Alpha          | 250                         | --  | --               | --   | --  | --               | --   | ND                                   | ND                     |
| 1,2-Dichloroethane                         |                | 500                         | 100                                       | 3                | 2  | 99  | 3                | 2  | 1                                    | 1                      |
| Benzene                                    |                | 500                         | 102                                       | 3                | 1  | 101                                       | 3                | 1  | 1                                    | 1                      |
| Fluorobenzene                              | Alpha          | 250                         | --  | --               | --   | --  | --               | --   | ND                                   | ND                     |
| 1,4-Difluorobenzene                        | Alpha          | 250                         | --  | --               | --   | --  | --               | --   | ND                                   | ND                     |
| Trichloroethene                            |                | 500                         | 71  | 10               | 6  | 86  | 8                | 5  | 2                                    | 2                      |
| 1,2-Dichloropropane- <i>d</i> <sub>6</sub> | Check          | 250                         | 93  | 2                | 3  | 94  | 2                | 2  | ND                                   | ND                     |
| 1,2-Dichloropropane                        |                | 500                         | 93  | 3                | 3  | 93  | 2                | 2  | 1                                    | 1                      |
| Methyl methacrylate                        |                | 500                         | 102                                       | 13               | 5  | 99  | 13               | 4  | 2                                    | 2                      |
| 1,4-Dioxane- <i>d</i> <sub>8</sub>         | Alpha          | 2500                        | --  | --               | --   | --  | --               | --   | ND                                   | ND                     |
| Bromodichloromethane                       |                | 500                         | 75  | 10               | 2  | 86  | 11               | 2  | 3                                    | 4                      |
| 1,4-Dioxane                                |                | 500                         | 115                                       | 3                | 22   | 108                                       | 3                | 11   | 3                                    | 2                      |
| Dibromomethane                             |                | 500                         | 92  | 4                | 4  | 99  | 4                | 3  | 1                                    | 1                      |
| 4-Methyl-2-pentanone                       |                | 1000                        | 128                                       | 20               | 8  | 108                                       | 21               | 6  | 3                                    | 2                      |
| <i>trans</i> -1,3-Dichloropropene          |                | 500                         | 61  | 36               | 2  | 61  | 36               | 2  | 1                                    | 2                      |

TABLE 10  
(continued)

| Compound                                     | Surrogate Type | Spike<br>(ppb) <sup>c</sup> | Using water standards <sup>a</sup>        |                  | Using tuna standards <sup>b</sup>          |   |                  |  | MDL vs.<br>Water<br>Std <sup>g</sup> | MDL vs.<br>Tuna<br>Std |
|--|----------------|-----------------------------|---|------------------|--|---|------------------|--|--------------------------------------|------------------------|
|  |                |                             | Mean<br>Compound<br>Recovery <sup>d</sup> | RSD <sup>e</sup> | Mean<br>Surrogate<br>Recovery <sup>f</sup> | Mean<br>Compound<br>Recovery <sup>d</sup> | RSD <sup>e</sup> | Mean<br>Surrogate<br>Recovery <sup>f</sup> |                                      |                        |
| Toluene- <i>d</i> <sub>8</sub>               | Beta           | 250                         | --  | --               | --   | --  | --               | --   | ND                                   | ND                     |
| Toluene                                      |                | 500                         | 101                                       | 4                | 4  | 98  | 4                | 2  | 2                                    | 1                      |
| Pyridine- <i>d</i> <sub>5</sub>              | Check/Alpha    | 2500                        | 51  | 25               | 25   | 72  | 16               | 21   | ND                                   | ND                     |
| Pyridine                                     |                | 500                         | 62  | 21               | 27   | 81  | 13               | 20   | 6                                    | 6                      |
| <i>cis</i> -1,3-Dichloropropene              |                | 500                         | 61  | 27               | 2  | 66  | 27               | 2  | 1                                    | 2                      |
| Ethyl methacrylate                           |                | 500                         | 100                                       | 12               | 5  | 95  | 12               | 4  | 1                                    | 1                      |
| <i>N</i> -Nitrosodimethylamine               |                | 3350                        | 657                                       | 28               | 39   | 160                                       | 30               | 10   | 208                                  | 100                    |
| 1,1,2-Trichloroethane- <i>d</i> <sub>3</sub> | Check          | 250                         | 80  | 6                | 4  | 93  | 6                | 3  | ND                                   | ND                     |
| 2-Hexanone                                   |                | 500                         | 141                                       | 23               | 9  | 114                                       | 23               | 7  | 1                                    | 1                      |
| 1,1,2-Trichloroethane                        |                | 500                         | 82  | 5                | 4  | 93  | 5                | 3  | 1                                    | 1                      |
| Tetrachloroethene                            |                | 500                         | 73  | 16               | 11   | 106                                       | 12               | 10   | 2                                    | 2                      |
| 1,3-Dichloropropane                          |                | 500                         | 99  | 2                | 5  | 97  | 2                | 3  | 1                                    | 1                      |
| Dibromochloromethane                         |                | 500                         | 61  | 11               | 3  | 90  | 19               | 3  | 6                                    | 8                      |
| 1,2-Dibromoethane- <i>d</i> <sub>4</sub>     |                | 250                         | --  | --               | --   | --  | --               | --   | ND                                   | ND                     |
| 2-Picoline                                   |                | 500                         | 163                                       | 16               | 38   | 131                                       | 11               | 16   | 7                                    | 7                      |
| 1,2-Dibromoethane                            |                | 500                         | 99  | 4                | 6  | 99  | 4                | 4  | 1                                    | 1                      |
| Chlorobenzene- <i>d</i> <sub>5</sub>         | Beta           | 250                         | --  | --               | --   | --  | --               | --   | ND                                   | ND                     |
| Chlorobenzene                                |                | 500                         | 95  | 3                | 6  | 99  | 3                | 4  | 1                                    | 1                      |
| 1,1,1,2-Tetrachloroethane                    |                | 500                         | 88  | 4                | 5  | 95  | 5                | 3  | 1                                    | 1                      |
| Ethylbenzene                                 |                | 500                         | 111                                       | 7                | 4  | 110                                       | 7                | 2  | 1                                    | 1                      |
| <i>N</i> -Nitrosomethylethylamine            |                | 3350                        | 516                                       | 31               | 31   | 182                                       | 27               | 7  | 71                                   | 33                     |
| <i>m+p</i> -Xylenes                          |                | 500                         | 107                                       | 6                | 4  | 107                                       | 6                | 2  | 1                                    | 1                      |
| Styrene                                      |                | 500                         | 94  | 3                | 4  | 95.7                                      | 3                | 3  | 2                                    | 1                      |
| <i>o</i> -Xylene- <i>d</i> <sub>10</sub>     |                | 250                         | --  | --               | --   | --  | --               | --   | ND                                   | ND                     |
| <i>o</i> -Xylene                             |                | 500                         | 102                                       | 4                | 4  | 101                                       | 4                | 3  | 1                                    | 1                      |
| Isopropylbenzene                             |                | 500                         | 116                                       | 16               | 8  | 124                                       | 15               | 6  | 1                                    | 1                      |

TABLE 10  
(continued)

| Compound                                   | Surrogate Type | Spike<br>(ppb) <sup>c</sup> | Using water standards <sup>a</sup>        |                  | Using tuna standards <sup>b</sup>          |   |                  | MDL vs.<br>Water<br>Std <sup>g</sup> | MDL vs.<br>Tuna<br>Std |  |
|--|----------------|-----------------------------|---|------------------|--|---|------------------|--------------------------------------|------------------------|--|
|  |                |                             | Mean<br>Compound<br>Recovery <sup>d</sup> | RSD <sup>e</sup> | Mean<br>Surrogate<br>Recovery <sup>f</sup> | Mean<br>Compound<br>Recovery <sup>d</sup> | RSD <sup>e</sup> |                                      |                        | Mean<br>Surrogate<br>Recovery <sup>f</sup> |
| Bromoform                                  | Check          | 500                         | 53  | 30               | 2  | 118                                       | 38               | 4                                    | 55                     | 163  |
| <i>cis</i> -1,4-Dichloro-2-butene          |                | 500                         | 5   | 134              | 0  | 5   | 134              | 0                                    | 45                     | 238  |
| <i>N</i> -Nitrosodiethylamine              |                | 3350                        | 356                                       | 31               | 62   | 168                                       | 28               | 18                                   | 24                     | 10   |
| 1,1,2,2-Tetrachloroethane                  |                | 500                         | 37  | 62               | 2  | 144                                       | 72               | 5                                    | 103                    | 664  |
| 4-Bromofluorobenzene                       |                | 250                         | 92  | 4                | 4  | 97  | 3                | 4                                    | 1                      | 2  |
| 1,2,3-Dichloropropane                      |                | 500                         | 103                                       | 10               | 5  | 98  | 11               | 4                                    | 4                      | 4  |
| Propylbenzene                              |                | 500                         | 113                                       | 17               | 10   | 125                                       | 16               | 8                                    | 2                      | 1  |
| <i>trans</i> -1,4-Dichloro-2-butene        |                | 500                         | 0   | 0                | 0  | 0   | 0                | 0                                    | 20                     | 37   |
| 1,3,5-Trimethylbenzene                     | Beta           | 500                         | 115                                       | 9                | 4  | 113                                       | 10               | 3                                    | 1                      | 1  |
| Bromobenzene- <i>d</i> <sub>5</sub>        |                | 250                         | --  | --               | --   | --  | --               | --                                   | ND                     | ND   |
| Bromobenzene                               |                | 500                         | 96  | 4                | 5  | 97  | 3                | 4                                    | 2                      | 2  |
| 2-Chlorotoluene                            |                | 500                         | 105                                       | 4                | 3  | 107                                       | 4                | 3                                    | 2                      | 2  |
| 4-Chlorotoluene                            |                | 500                         | 101                                       | 4                | 3  | 104                                       | 5                | 3                                    | 2                      | 2  |
| Pentachloroethane                          |                | 500                         | 28  | 54               | 1  | 135                                       | 75               | 5                                    | 0                      | 0  |
| <i>tert</i> -Butylbenzene                  |                | 500                         | 118                                       | 19               | 10   | 126                                       | 19               | 8                                    | 2                      | 1  |
| 1,2,4-Trimethylbenzene                     |                | 500                         | 112                                       | 9                | 5  | 107                                       | 10               | 4                                    | 1                      | 1  |
| <i>sec</i> -Butylbenzene                   | Beta           | 500                         | 114                                       | 24               | 15   | 134                                       | 22               | 13                                   | 2                      | 1  |
| Aniline                                    |                | 500                         | 80  | 36               | 37   | 57  | 38               | 15                                   | 9                      | 14   |
| <i>p</i> -Isopropyltoluene                 |                | 500                         | 124                                       | 21               | 16   | 127                                       | 20               | 12                                   | 2                      | 1  |
| 1,3-Dichlorobenzene                        |                | 500                         | 94  | 5                | 7  | 98  | 4                | 5                                    | 1                      | 1  |
| 1,4-Dichlorobenzene                        |                | 500                         | 93  | 6                | 7  | 96  | 5                | 6                                    | 1                      | 1  |
| <i>n</i> -Butylbenzene                     |                | 500                         | 109                                       | 22               | 17   | 128                                       | 20               | 15                                   | 2                      | 1  |
| 1,2-Dichlorobenzene- <i>d</i> <sub>4</sub> |                | 250                         | --  | --               | --   | --  | --               | --                                   | ND                     | ND   |
| 1,2-Dichlorobenzene                        |                | 500                         | 91  | 10               | 10   | 96  | 9                | 7                                    | 2                      | 2  |
| Decafluorobiphenyl                         | Beta           | 250                         | --  | --               | --   | --  | --               | ND                                   | ND                     |  |
| <i>N</i> -Nitrosodi- <i>n</i> -propylamine |                | 3350                        | 288                                       | 51               | 47   | 179                                       | 50               | 21                                   | 35                     | 20   |

TABLE 10  
(continued)

| Compound                                      | Surrogate Type | Spike<br>(ppb) <sup>c</sup> | Using water standards <sup>a</sup>        |                  | Using tuna standards <sup>b</sup>          |   |                  |  | MDL vs.<br>Water<br>Std <sup>g</sup> | MDL vs.<br>Tuna<br>Std |
|---|----------------|-----------------------------|---|------------------|--|---|------------------|--|--------------------------------------|------------------------|
|   |                |                             | Mean<br>Compound<br>Recovery <sup>d</sup> | RSD <sup>e</sup> | Mean<br>Surrogate<br>Recovery <sup>f</sup> | Mean<br>Compound<br>Recovery <sup>d</sup> | RSD <sup>e</sup> | Mean<br>Surrogate<br>Recovery <sup>f</sup> |                                      |                        |
|   |                |                             |   |                  |  |   |                  |  |                                      |                        |
| Nitrobenzene- <i>d</i> <sub>5</sub>           | Check          | 250                         | 374                                       | 105              | 283  | 176                                       | 58               | 40   | ND                                   | ND                     |
| Acetophenone- <i>d</i> <sub>5</sub>           | Check          | 1000                        | 216                                       | 47               | 29   | 187                                       | 47               | 19   | ND                                   | ND                     |
| <i>o</i> -Toluidine                           |                | 3350                        | 67  | 39               | 34   | 58  | 41               | 18   | 62                                   | 103                    |
| 1,2-Dibromo-3-chloropropane                   |                | 500                         | 97  | 39               | 12   | 107                                       | 40               | 10   | 31                                   | 42                     |
| Hexachlorobutadiene                           |                | 500                         | 108                                       | 27               | 20   | 122                                       | 28               | 18   | 4                                    | 3                      |
| 1,2,4-Trichlorobenzene- <i>d</i> <sub>3</sub> | Beta           | 250                         | --  | --               | --   | --  | --               | --   | ND                                   | ND                     |
| 1,2,4-Trichlorobenzene                        |                | 500                         | 94  | 12               | 14   | 94  | 9                | 11   | 4                                    | 6                      |
| Naphthalene- <i>d</i> <sub>8</sub>            | Check          | 500                         | 85  | 14               | 18   | 93  | 12               | 14   | ND                                   | ND                     |
| Naphthalene                                   |                | 1000                        | 95  | 11               | 22   | 95  | 9                | 16   | 5                                    | 3                      |
| 1,2,3-Trichlorobenzene                        |                | 500                         | 88  | 8                | 23   | 96  | 9                | 18   | 10                                   | 13                     |
| <i>N</i> -Nitrosodibutylamine                 |                | 3350                        | 25  | 99               | 19   | 25  | 115              | 12   | 79                                   | 15                     |
| 2-Methylnaphthalene                           |                | 3350                        | 194                                       | 21               | 74   | 96  | 23               | 26   | 159                                  | 50                     |
| 1-Methylnaphthalene- <i>d</i> <sub>10</sub>   | Beta           | 1000                        | --  | --               | --   | --  | --               | --   | ND                                   | ND                     |

<sup>a</sup>Calibration standards were prepared using 5 mL of water as the matrix.

<sup>b</sup>Calibration standards were prepared using 1 g of tuna as the matrix.

<sup>c</sup>1-g samples were spiked, mixed ultrasonically, and allowed to equilibrate overnight (>1000 min) prior to analysis.

<sup>d</sup>Average percent recovery of seven replicate analyses of fish tissue taken from canned, water-packed tuna.

<sup>e</sup>Relative standard deviation

<sup>f</sup>Method detection limits reported here were calculated as three times the standard deviation of four replicate analyses.

ND = Not determined

Int = Spectral interferences prevented accurate integrations.

Cont = The spike could not be distinguished from the background levels.

TABLE 11A  
EXAMPLE SURROGATE DATA

| <b>First Pass Relative Volatility vs. Recovery</b><br>(Used to Estimate Relative Volatility Effects on BP Surrogates) |               |                     |              |
|---|---------------|---------------------|--------------|
| Compound  | Boiling Point | Relative Volatility | Recovery (%) |
| Fluorobenzene   | 40            | 3.5                 | 99.1         |
| 1,2-Dichloroethane- $d_4$   | 37            | 20.0                | 101.2        |
| <b>Recovery vs. Boiling Point</b><br>(First-Pass Relative Volatility Corrections)                                     |               |                     |              |
| Compound  | Boiling Point | Relative Volatility | Recovery (%) |
| Toluene- $d_8$  | 111           | 4.28                | 102.0        |
| Chlorobenzene- $d_5$  | 131           | 6.27                | 101.3        |
| Bromobenzene- $d_5$   | 155           | 7.93                | 102.8        |
| 1,2-Dichlorobenzene- $d_4$  | 181           | 8.03                | 103.2        |
| Decafluorobiphenyl  | 206           | 3.03                | 103.3        |
| 1,2,4-Trichlorobenzene- $d_3$   | 213           | 7.88                | 102.8        |
| 1-Methylnaphthalene- $d_{10}$   | 241           | 67.00               | 94.0         |
| Slope (% per degree)  | 0.000143      |                     |              |
| Recovery at 140°C   | 102.2%        |                     |              |
| Correction coefficient  | 0.758352      |                     |              |
| <b>Recovery (BP corrected) vs. Relative Volatility</b>  |               |                     |              |
| Compound  | Boiling Point | Relative Volatility | Recovery (%) |
| Hexafluorobenzene   | 82            | 0.86                | 99.7         |
| Pentafluorobenzene  | 85            | 1.51                | 99.2         |
| Fluorobenzene   | 85            | 3.50                | 98.8         |
| 1,4-Difluorobenzene   | 89            | 3.83                | 98.7         |
| <i>o</i> -Xylene- $d_{10}$  | 143           | 6.14                | 100.0        |
| Chlorobenzene- $d_5$  | 131           | 6.27                | 99.5         |
| 1,2-Dichloroethane- $d_4$   | 84            | 20.00               | 100.9        |
| 1,2-Dibromoethane- $d_4$  | 131           | 26.00               | 101.6        |
| Tetrahydrofuran- $d_{10}$   | 66            | 355.00              | 103.7        |
| 1,4-Dioxane- $d_8$  | 101           | 5800.00             | 97.0         |
| Pyridine- $d_5$   | 101           | 15000.00            | 76.2         |
| Slope (% per ln[rel. vol.])   | -0.01363      |                     |              |
| Recovery at 140°C   | 98.2%         |                     |              |
| Correction coefficient  | 0.370579      |                     |              |

TABLE 11B  
EXAMPLE OF THE ACCURACY OF THE CHECK SURROGATES

| Accuracy of Check Surrogates                 |                |                     |                       |           |     |                    |     |                    |     |
|--|----------------|---------------------|-----------------------|-----------|-----|--------------------|-----|--------------------|-----|
| Compound                                     | Boiling Point  | Relative Volatility | Measured Recovery (%) | Predicted |     | Measured/Predicted |     | Predicted/Measured |     |
|  |                |                     |                       | Recovery  | SD  | Recovery           | SD  | Accuracy           | SD  |
| Purgeable volatiles                          |                |                     |                       |           |     |                    |     |                    |     |
| Benzene- <i>d</i> <sub>6</sub>               | 79             | 3.92                | 100.2                 | 98.8      | 0.1 | 101.4              | 0.1 | 98.6               | 0.1 |
| Methylene chloride                           | 40             | 11.10               | 101.7                 | 100.2     | 0.2 | 101.5              | 0.2 | 98.5               | 0.2 |
| 1,2-Dichloropropane- <i>d</i> <sub>6</sub>   | 95             | 11.00               | 101.1                 | 100.9     | 0.4 | 100.2              | 0.3 | 99.8               | 0.3 |
| 1,1,2-Trichloroethane- <i>d</i> <sub>3</sub> | 112            | 26.60               | 103.4                 | 102.9     | 0.7 | 100.4              | 0.6 | 99.6               | 0.6 |
| 4-Bromofluorobenzene                         | 152            | 8.05                | 102.9                 | 102.4     | 0.4 | 100.6              | 0.3 | 99.4               | 0.3 |
|  | Mean ± 1 sigma |                     | 101.9 ± 1.2           | 101.0     | 1.5 | 100.8              | 0.5 | 99.2               | 0.5 |
| Semivolatiles                                |                |                     |                       |           |     |                    |     |                    |     |
| Naphthalene- <i>d</i> <sub>8</sub>           | 217            | 18.00               | 104.6                 | 102.7     | 1.1 | 101.8              | 1.1 | 98.2               | 1.0 |
| Nitrobenzene- <i>d</i> <sub>5</sub>          | 210            | 87.50               | 107.1                 | 104.7     | 2.7 | 102.3              | 2.6 | 97.7               | 2.5 |
| Acetophenone- <i>d</i> <sub>5</sub>          | 202            | 161.00              | 103.1                 | 107.3     | 0.2 | 96.1               | 0.2 | 104.0              | 0.2 |
|  | Mean ± 1 sigma |                     | 104.9 ± 1.6           | 104.9     | 8.3 | 100.1              | 3.2 | 100.0              | 2.9 |
| Non-purgeable volatiles                      |                |                     |                       |           |     |                    |     |                    |     |
| Ethyl acetate- <sup>13</sup> C <sub>2</sub>  | 77             | 150.00              | 106.0                 | 104.0     | 0.1 | 101.9              | 0.1 | 98.1               | 0.1 |
| Acetone- <i>d</i> <sub>6</sub>               | 57             | 600.00              | 106.5                 | 103.2     | 0.1 | 103.2              | 0.1 | 96.9               | 0.1 |
| Pyridine- <i>d</i> <sub>5</sub>              | 115            | 15000.00            | 77.6                  | 82.7      | 5.3 | 93.9               | 6.0 | 106.5              | 6.8 |
|  | Mean ± 1 sigma |                     | 96.7 ± 13.5           | 96.7      | 7.0 | 99.6               | 2.9 | 100.5              | 4.3 |



FIGURE 1  
DIAGRAM OF VACUUM DISTILLATION APPARATUS

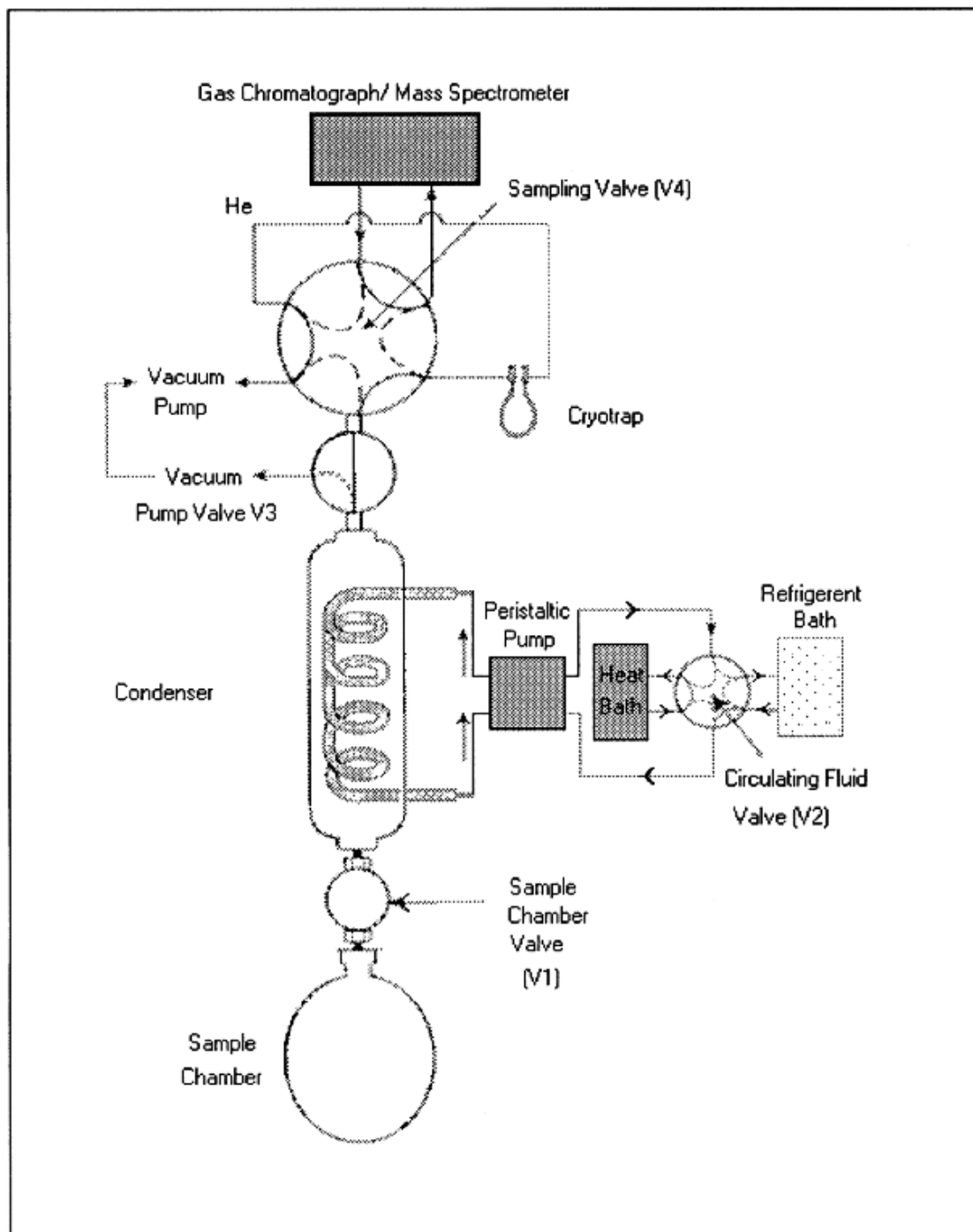
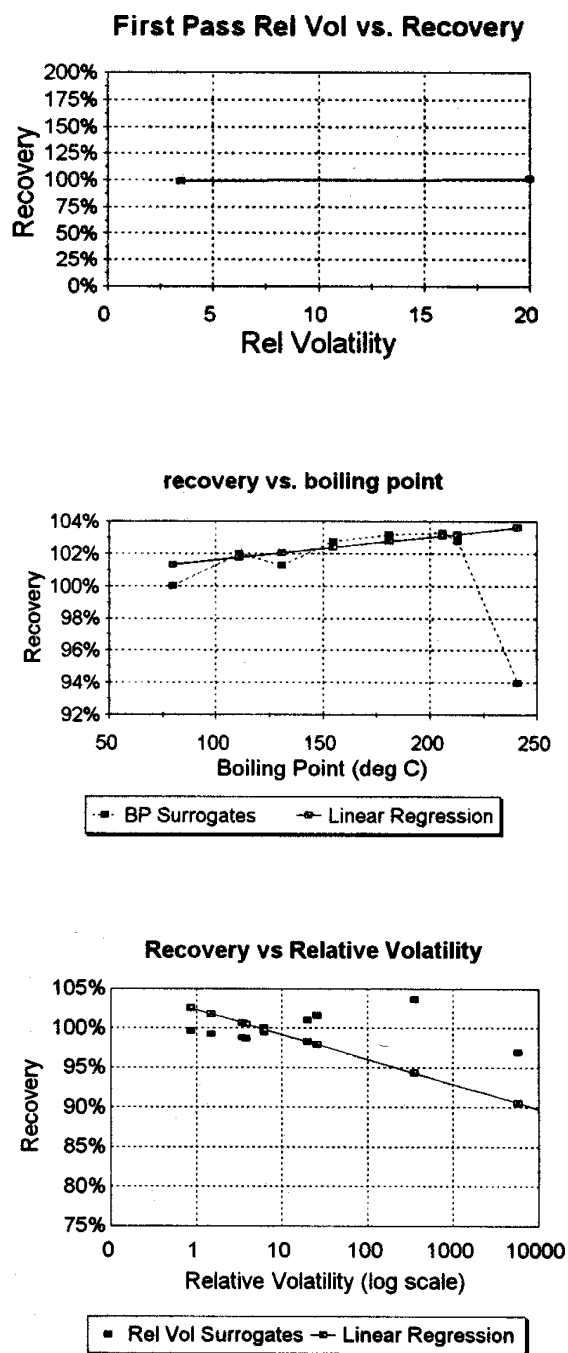
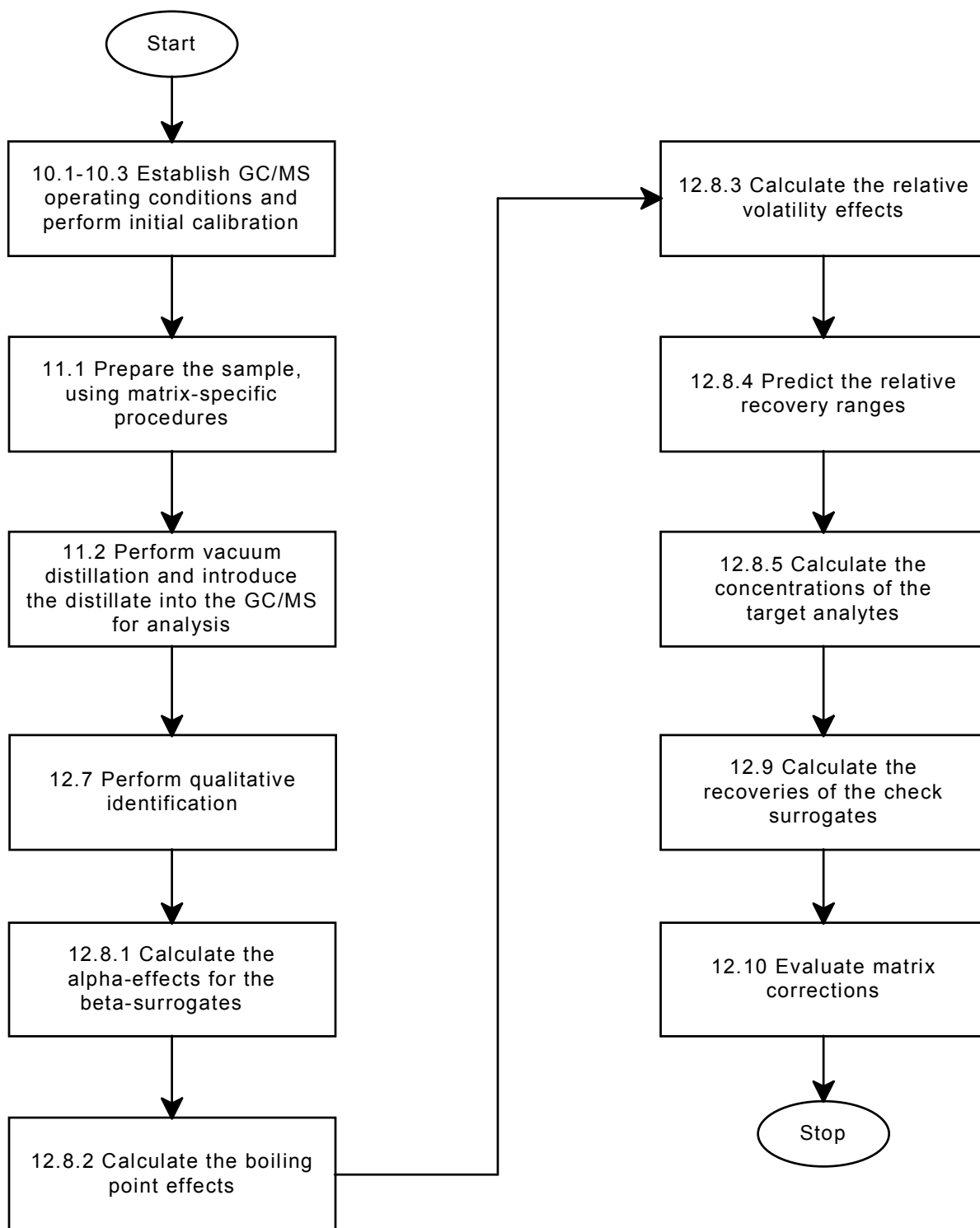


FIGURE 2

EXAMPLE SURROGATE RECOVERY CORRECTION GRAPHS



These graphs illustrate the effects of recovery corrections based on relative volatility and boiling point on the results for the target analytes from a 5-mL water sample. Such graphs, in conjunction with the check surrogate data themselves, may provide a means to identify matrix effects, including those related to specific analytes. See Tables 11A and 11B for examples of the surrogate data.

VOLATILE ORGANIC COMPOUNDS BY VACUUM DISTILLATION GC/MS

## GLOSSARY

$\alpha$ -effect - The effect of the matrix on the relative volatility of a compound.

$\alpha$ -surrogate - see Gas-liquid partitioning surrogate.

$\beta$ -effect - The effect of the matrix on recovery as a function of boiling point of a compound. Also known as boiling point effects.

$\beta$ -surrogates - See condensation surrogates.

Class I compounds - Those compounds with boiling points generally below 160°C and  $\alpha$ -values (or K-values) below 50. Class I compounds include the permanent gases and most volatiles.

Class II compounds - Those with boiling points greater than 160 °C. Class II compounds include the neutral semivolatiles.

Class III compounds - Those with  $\alpha$ -values greater than 50. Class III compounds include the water-soluble volatiles.

Class IV compounds - The basic compounds that are susceptible to degradation and have a low detector response. Class IV compounds include the basic semivolatiles.

Condensation surrogates (boiling point or  $\beta$ -surrogates) - The  $\beta$ -surrogates are added to the sample to measure the recovery of analytes relative to how the compounds condense on apparatus and sample surfaces during a vacuum distillation. The  $\beta$ -surrogates are presented in Table 3.

Distillation performance surrogates - See gas-liquid partitioning surrogates.

Gas-liquid partitioning surrogates ( $\alpha$ -surrogates) - The  $\alpha$ -surrogates are added to the sample to measure the recovery of analytes relative to how the compound partitions between gas and liquid (partition coefficient K). Compounds that are going to be used as  $\alpha$ -surrogates that have boiling points above 40°C must first be evaluated for potential losses due to condensation and a correction made to their recoveries when condensation is evident.  $\alpha$ -surrogates are also known as distillation performance surrogates.

Relative volatility ( $\alpha$ ) - The property of an analyte that determines its presence in the vapor phase above an aqueous sample. The relative volatility is proportional to the gas-liquid partition coefficient (K) of the compound. Either  $\alpha$ - or K-values can be used to describe this effect and Table 3 lists  $\alpha$ -values for the compounds in Table 1 that are equivalent to K (Reference 7).